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TEXT-BOOKS OF CHEMICAL RESEARCH AND ENGINEERING

AN INTRODUCTION TO THE PHYSICS AND CHEMISTRY OF COLLOIDS

BY

EMIL HATSCHEK

Fourth Edition

Entirely Re-written and Enlarged

With 20 Illustrations

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PREFACE TO FOURTH EDITION

THE present edition has been entirely rewritten and, incidentally, enlarged. The changes made are partly the outcome of increased experience in teaching the subject, and partly caused by the inclusion of important recent work on fundamental aspects of the science. The literature up to the middle of the present year has been drawn upon, as far as it falls within the purview of the present book; references are given to such papers as have not found their way into the majority of text-books. At the same time the author has endeavoured to preserve the general character of the work.

As Laboratory Manuals of Colloid Chemistry are now available, the short appendix on experimental technique added to the third edition has been omitted.

EMIL HATSCHEK.

LONDON, *October*, 1921.

PREFACE TO FIRST EDITION.

THE present work is a slightly enlarged reprint of a series of articles published in *The Chemical World*, which in their turn were based on a course of ten lectures delivered at the Sir John Cass Technical Institute to students of very varied attainments and interested in every branch of chemistry and of chemical industry. The book accordingly does not aim at a completeness precluded alike by its compass and the extremely vigorous growth of the subject, but is only intended to introduce readers with a reasonable knowledge of physics and chemistry to the fundamental facts and methods of a branch of physical chemistry on the importance of which it is hardly necessary to insist.

Certain features in the selection of subjects and in the order of presenting them, which will be apparent to readers familiar with the existing literature, are due to a vivid recollection of the difficulties experienced by the author in his first studies, and the desire to spare the student as many of these as appear avoidable. Those desirous of ampler and more detailed information are referred to Wolfgang Ostwald's "Grundriss der Kolloidchemie" and H. Freundlich's "Kapillarchemie," English translations of which are urgently required.

EMIL HATSCHEK.

LONDON, 1913.

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AN INTRODUCTION TO THE PHYSICS AND CHEMISTRY OF COLLOIDS.

CHAPTER I.

THE first systematic investigation of our subject, and the name "Colloids," are due to Thomas Graham, whose results were published in a series of papers between 1861 and 1864. These fundamental researches have so far not been republished in English, but some of them have been included by Wilhelm Ostwald in his collection of "Klassiker der exakten Wissenschaften." Graham's discoveries may be briefly summarised under two heads. In studying dialysis, *i.e.*, the diffusion of dissolved substances through organic membranes like parchment into the pure solvent, he found that some of them passed freely through the membrane into the surrounding solvent, while a number of others failed to do so, or diffused at an extremely slow rate. Generally speaking, the former were bodies which were known to crystallize, while the latter, *e.g.*, albumin, gelatin, gum-arabic, etc., were known only in the amorphous condition. Graham accordingly divided soluble substances into two classes: Crystalloids and Colloids (from *colla*, glue).

The second discovery made by Graham in prosecuting these researches was that a number of

substances generally known as insoluble could, by appropriate methods, be obtained in what at first sight appeared to be real solutions. These methods will be discussed in detail later on, but it may be mentioned here that Graham obtained, and very carefully investigated, such solutions of silicic acid, tungstic acid and a number of basic hydroxides, like those of iron, chromium and aluminium. Most of these appeared to the eye like true solutions, *i.e.*, they were perfectly clear and apparently homogeneous. They did, however, not diffuse through parchment, and on account of this property were called by Graham "colloidal solutions," or simply "sols," which term has now become generally accepted. These sols showed a further striking peculiarity, which distinguished them sharply from true solutions such as, say, cane sugar or sodium chloride solutions, inasmuch as very small additions of electrolytes, which did not react at all with the dissolved substance, caused radical alterations in the condition of the sols. Traces of carbon dioxide, for instance, caused the silicic acid sol to set to a translucent jelly, while small additions of any neutral salt would precipitate the ferric hydroxide as a flocculent mass. These transformation products of sols were called "gels" by Graham, a title still in use, though generally employed in a restricted sense.

While Graham's investigations were the first ones directed systematically towards the production of sols and the application to them of dialysis, both as a means of preparation and as a test, numerous earlier observations of sol formation, *i.e.*, the production of apparent solutions of substances known as insoluble, are not wanting even in the early days of chemistry. Between 1808 and 1833 Berzelius had observed what would now be called sols of sulphur and arsenious sulphide, of "b-" silicic acid, tellurium, etc. Sulphur sols, obtained by the reaction between hydrogen

sulphide and sulphur dioxide in aqueous solution, were investigated carefully by Wackenroder (1846), and by Selmi and Sobrero (1850). They were again studied by Debus (1888), who remarked on the similarity between them and the sols of Thomas Graham.

Of particular interest, in view of the great theoretical importance which they ultimately acquired, is the history of the metal sols. Red or purple liquids, obtained by the reduction of gold chloride, were known to the alchemists and were used medicinally under the title of "*aurum potabile*." Various directions for making the latter are given in Marcquer's "Dictionnaire de Chymie" as late as 1774. The earliest reference in English literature is probably a somewhat tantalizing entry in the Diary of John Evelyn, who writes on June 27th, 1653: "Monsieur Roupel sent me a small phial of his *aurum potabile*, with a letter showing the way of administering it, and the stupendous cures it had don at Paris; but ere it came to me, by what accident I know not, it had all run out."

In 1839 Wöhler found that silver citrate heated in a stream of hydrogen left a residue which dissolved in water with a red colour. The experiment was repeated and frequently referred to in the dispute regarding the existence of silver "sub"-salts, as which Wöhler had regarded the substance obtained by him. In 1887 Muthmann repeated the experiment, dialyzed the red solution and showed that the red substance did not pass through the membrane, but that only undecomposed silver citrate could be found in the outside water. This investigation is of great interest as being the first one in which dialysis was applied to a metal sol. Carey Lea (1889) developed various methods for the reduction of silver which yielded sols of high concentration; analysis showed the coagulum from these sols to be silver with a consi-

derable admixture of the other reaction products, and Carey Lea described it as " allotropic silver."

To return to gold sols, a considerable step in advance was made by Faraday (1857), who obtained violet and purple liquids by reducing very dilute solutions of gold chloride with ethereal solutions of phosphorus. He definitely expressed the view that they owed their colour to metallic gold in a state of fine division, noted the effect of small quantities of electrolytes and even the influence of the glass vessels on the stability of his preparations. Some of them are preserved at the Royal Institution, and one or two specimens still retain a faint tinge of colour, while the rest have coagulated. A further observation made by Faraday, that " a little jelly " increased the stability of his preparations, has also been confirmed by subsequent investigations and has acquired considerable importance.

The modern history of gold sols may be said to begin with Zsigmondy's paper on " Aqueous Solutions of Metallic Gold," published in 1898. This describes the method, now classical, of reducing alkaline gold chloride solution with formaldehyde and is the first research directed towards the production of definite and reproducible gold sols of bright red colour. The question of the state of the metal in these solutions was definitely settled by their examination in the ultra-microscope, invented by Zsigmondy and Siedentopf (1903).

The last decade of the nineteenth and the beginning of the present century saw a considerable amount of fundamental work on aspects of the subject other than the preparation of sols. Among the most important must be mentioned the investigations on the effects of electrolytes by Linder and Picton (1892) and Hardy (1900). Research was greatly stimulated by the invention of the ultra-microscope, and in 1909 and 1910 the first works dealing comprehensively

and systematically with the great mass of uncoordinated material which had accumulated by then were published by R. Zsigmondy, Wolfgang Ostwald and H. Freundlich.

The principal advance made since Graham's fundamental work has been the proof, now quite conclusive, that there are no " Colloids " in Graham's sense, *i.e.*, no definite class of substances endowed with the peculiar properties designated by that term, but that by suitable methods *any substance can, in a suitable medium, be prepared in a colloidal condition*, which thus presents itself as a *state*, not as a *form* of matter. Thus sodium chloride is certainly a very well-defined crystalline substance, yet colloidal solutions of it in organic solvents can be obtained by several methods.

P. P. von Weimarn was the first to formulate the conditions necessary for obtaining a given body in colloidal solution and succeeded in preparing sols of several hundred substances. Most of the metals and many non-metallic elements have been obtained in the colloidal state, and sols of silver, mercury, sulphur, selenium, etc., are made commercially and are used in medicine. Even the alkali metals have been obtained in the colloidal state by Svedberg, by the use of organic solvents, very low temperature and experimental arrangements of great ingenuity. Similarly, a large number of hydroxide and sulphide sols are known, some of which have been the subjects of classical investigations, to which we shall have occasion to refer extensively.

All these sols of inorganic bodies are laboratory products prepared by certain well-defined methods, the principles of which will become clear as we study their properties. Like many laboratory products in the domain of both inorganic and organic chemistry they have been of the greatest value in enabling us to form theoretical conceptions. Apart from the

fundamental characteristic of not diffusing through membranes like parchment, they have another property in common: on the addition of varying, but generally small quantities of electrolytes, they undergo marked and largely irreversible changes, the dissolved substance being precipitated or the whole liquid setting to a jelly.

In striking contrast to these artificially prepared products there exists a large group of substances, which can be dissolved at once without special methods to form colloidal solutions and are not, indeed, known to form any others or to occur in the crystalline state. This comprises the materials from which all living organisms are built up, like the proteins, cellulose, starch and many other carbohydrates; also the various esters of cellulose, indiarubber, many dyes, etc. Some of these, like several proteins, dissolve in water alone; cellulose is dissolved by aqueous solutions of copper oxide-ammonia, zinc chloride or calcium thiocyanate; while the cellulose esters and indiarubber require suitable organic solvents. Even the substances which form sols with water differ considerably in their individual behaviour. Some, like gelatin, form sols only above a certain temperature; when this falls below a limit depending on various factors, the sol sets to a gel, the process being reversible, *i.e.*, the gel "melts" again to a sol on warming. On the other hand, egg albumin is soluble at ordinary temperatures, but on heating above 62° C. coagulates to an insoluble mass. Gum-arabic, to mention a third substance belonging to this class, forms a viscous sol which neither sets to a gel on cooling nor coagulates on heating. Similarly varied is the behaviour of these organic colloids towards electrolytes, but they all share with one another and with the inorganic sols the fundamental characteristic of not diffusing through parchment or similar membranes.

As regards the sols in organic solvents, it must be mentioned that the criterion of dialysis has hardly been applied to them except in isolated cases. At the same time we have, in the instances quoted, sufficient evidence of other kinds to the colloidal condition of those substances. One of these characteristics is an extremely low osmotic pressure ; in many cases this is not measurable either directly or by the usual indirect methods (lowering of vapour pressure or of freezing point), while in others very small pressures are observed, which are strikingly affected by the method of preparation and by small admixtures.

While the recognition of the general possibility of the colloidal state—into which all substances that do not assume it spontaneously can be brought by suitable and well-defined methods—constitutes the first great advance since Graham's time, a step of equal importance is the demonstration that the colloidal state is only a special case of the " disperse system," a concept and term first introduced by Wolfgang Ostwald. A disperse system is a system of two phases differing in one or more physical properties, and having a large surface of contact, or interface. To obtain a surface large in proportion to the volume of at least one phase, it is necessary to reduce one or more linear dimensions of the latter : if one is so reduced, we have films ; if two, filaments ; and if all three are small, particles bounded by a closed surface, *e.g.*, spherical, of one phase distributed in the other. All three configurations occur in nature in many variations ; the type of most immediate interest to us is the third. In such a system we can obviously pass in the one phase from one point to any other, without encountering the particles of the other phase ; the former is therefore called the *continuous* (or " closed ") *phase*, or frequently the *dispersion medium*, while the particles constitute the *disperse phase*.

While a difference in one or more physical properties of the two phases, *i.e.*, heterogeneity, is part of the definition, it must not be overlooked that the phases may, nevertheless, have one such property in common. For example, a suspension of glass in cedar oil of the same refractive index is optically homogeneous, although heterogeneous in all other respects; while a suspension of particles in a liquid of the same density will be homogeneous as far as the effects of gravity or centrifugal force go, while its optical heterogeneity may be obvious even without the use of instruments. A single criterion is therefore never sufficient to settle this question definitely, a point which is sometimes overlooked, as we shall have occasion to remark later on.

Differences in any one physical property could of course form the basis of a classification of disperse systems, but the one which has found most general acceptance is that introduced by Wolfgang Ostwald, which differentiates the disperse systems according to the *state of aggregation* of the phases, *i.e.*, whether solid, liquid or gaseous. As both phases may be in the same state, nine cases altogether are possible, of which one, however, is strictly limited—that in which both phases are gaseous. Since gases are miscible in all proportions, we cannot have "particles" of disperse phase larger than molecules. The other eight types are set out below; the last column gives examples of such systems in the terms in which the principal representatives are generally described.

	Dispersion medium.		Disperse phase.		
1.	Gas	..	Liquid	..	Fog, mist.
2.	Gas	..	Solid	..	Smoke, fine dust.
3.	Liquid	..	Gas	..	Froth, foam.
4.	Liquid	..	Liquid	..	Emulsions.
5.	Liquid	..	Solid	..	Suspensions.

	Dispersion medium.		Disperse phase.	
6.	Solid	..	Gas	.. "Solid" froths, *e.g.*, pumice stone, etc.
7.	Solid	..	Liquid	.. Numerous minerals.
8.	Solid	..	Solid	.. Ruby glass, many coloured minerals.

Of the above, 4 and 5 will prove to be of the most immediate interest to us. Investigation has shown that these systems exhibit the striking features of the colloidal state when the size of the particles falls between certain well-defined limits, and that this is principally due to the increase of interface consequent on the reduction of linear dimensions. A simple numerical example will illustrate this increase. If we imagine a volume of 1 c.c. of any material contained in a cube of 1 cm. edge, the total surface will be 6 sq. cm. If we reduce the linear dimension to one-tenth, *i.e.*, if we divide the cubic centimetre of material into cubes having an edge of 1 mm. we obtain 1,000 cubes, each having a surface of 6 sq. mm., so that the total surface is now 6,000 sq. mm. = 60 sq. cm., or ten times the surface of the original cube with 1 cm. edge. The surface therefore increases in the same ratio in which the linear dimension is reduced. If we subdivide the cubic centimetre into cubes with an edge of 1 μ (this is the usual unit for *microscopic* measurements) = 0·001 mm. = 1×10^{-4} cm., the total surface will be 6×10^{4} sq. cm. = 6 *square metres*. It will thus be realized that still further subdivision leads to such an increase in surface per unit mass that certain energies, of which surfaces are the seat, may affect the character of the disperse system to an extent equal with, or even greater than, that of the specific properties of the disperse phase in mass. The surface per unit volume of

disperse phase has been called by Ostwald the *specific surface*.

The concept of the disperse system is an important generalization and enables us, *inter alia*, to trace a more or less continuous transition from colloidal solutions to coarser systems in the one direction and to " molecular " and " ionic " disperse systems, *i.e.*, true solutions, in the other. At the same time, its bearing on the subject will be more easily grasped if, instead of attempting to apply it *a priori*, we proceed to study the methods by which colloidal solutions have been examined and to learn how the results thus obtained have led to definite conclusions regarding the size and state of the disperse phase.

Before entering upon this closer study, it may be well to answer two questions, which will naturally suggest themselves to the reader who has had no practical experience of the subject: how is it possible to tell whether a given solution contains colloids? and how can a few typical sols be easily prepared?

As regards the first question, the fundamental method is still dialysis. Full details for carrying out this, as well as for preparing a number of standard sols, are given in the author's " Laboratory Manual " (1st edition, 1920), to which the reader is referred for experimental procedure and technique generally. For those unable to devote much time to experimental work, the following directions will be sufficient:—

The simplest contrivance for dialysing aqueous solutions is a bag of parchment paper. A hexagonal or circular sheet, previously well soaked in distilled water, is folded over the bottom of a beaker and a string tied round it loosely. The bag is then slipped off the beaker, and a string threaded through the folds near the mouth, by which it is suspended over some convenient vessel so that the bottom of the bag

comes well within the latter. The outside vessel is now filled with water up to the bottom of the bag, the solution to be dialysed poured slowly into the latter and water added outside, until the levels inside and outside the dialyser are approximately the same. The outside water is changed at intervals until it remains pure, which is ascertained by the colour or by tests with suitable reagents. Whatever is then left inside the dialyser is in colloidal solution.

The following sols, which are extremely easy to prepare, may serve as representatives of important types :—

Copper ferrocyanide sol.—Prepare solutions of copper sulphate and of potassium ferrocyanide, each containing 0·75 gm. per litre of the crystallized salts. Pour a measured volume of the former into an equal volume of the latter with constant stirring. A clear brown liquid results, which will keep for a long time in stoppered flasks of good glass.

Albumin sol.—Dissolve 5 gm. of dried egg albumin in 100 c.c. of 0·7 per cent. solution of sodium chloride. Allow to stand over night and then filter through a soft filter paper. If the sol is to be kept, it must receive a small addition of thymol, to prevent putrefaction.

Gelatin sol and gel.—Soak 10 gm. of leaf gelatin, broken into small pieces, in 100 gm. of water over-night. Warm on the water bath until the whole has dissolved. Above about 27° C. the system forms the sol; below that temperature it sets to a reversible gel, *i.e.*, on warming it is again transformed into sol. This preparation must also be preserved with a little thymol.

By dialysing the ferrocyanide or the albumin sol it can at once be shown that they conform to our first test, *i.e.*, that they do not diffuse through the parchment membrane. In the former case the outside water remains colourless; in the latter it

can be shown by any of the well-known protein reactions to be free from albumin. The effect of electrolytes on the ferrocyanide sol may also be easily demonstrated by adding to 10 c.c. of it a few drops of almost any salt solution to be found on the laboratory shelves; the sol immediately becomes turbid, and after a few hours the ferrocyanide deposits as a flocculent precipitate.

CHAPTER II.

In the preceding chapter some general characteristics of colloidal solutions, more particularly their failure to diffuse through membranes, have been briefly referred to. It now remains to describe in some detail the methods applied to the investigation of colloids in more recent times, and to see what conclusions as to the nature of the colloidal state, or, in other words, the difference between true and colloidal solutions, can be drawn from the results obtained by these various methods.

As regards dialysis, we find that parchment paper and certain other septa, like collodion films, many animal membranes, etc., allow the passage of true solutes, *i.e.*, of substances present in the solvent as molecules or as ions, while they retain colloids. If we ask ourselves for the reason of this phenomenon, the simplest answer—though by no means a complete one—is obviously that the colloids are present as particles or aggregates too large to pass through the pores in the membrane. They may, of course, actually have molecules of such excessive size—thus Congo Red, a dye which lies on the border between true and colloidal solutions, has a molecule consisting of 72 atoms with a molecular weight of 654—and bodies which also form spontaneously colloidal solutions, like albumin and other proteins, certainly have molecules of still more considerable size. On the other hand, this explanation seems hardly applicable to the inorganic and particularly the metal sols, and it is necessary to assume that these contain aggregates formed of a large number of

molecules—an assumption for which, as we shall see later on, there is now direct experimental evidence.

It is, however, impossible to look on dialysis as a simple "sieve" action of the septum, because certain little understood relations between the solvent and the membrane are necessary to permit the latter to pass even solvent alone. Even if it were possible, the fact that dialysis is carried on without any pressure would make conclusions uncertain: it is quite usual to retain by ordinary filter media under low pressure particles that are much smaller than the pores of the former; thus sand filters retain bacteria, although they are very much smaller than the interstices between the sand grains. To eliminate this difficulty, and also with the purpose of separating the *disperse phase from the dispersion medium*, and not only from the true solutes which may be present, various investigators have attempted to retain colloids by filtration under pressure through very dense media, such as the filter candles used in bacteriological work. Linder and Picton used the latter in the course of their classical investigations on arsenic trisulphide sols, which were found to vary according to the method of preparation. Most of them passed through the filter unaltered, but a portion of the sulphide from certain sols was retained. For these isolated cases a limit value for the size of the particles could thus be deduced.

A step in advance was taken by C. J. Martin, who used as filtering media gels, *e.g.*, of silicic acid, and employed very considerable pressure. He found it possible by this procedure to retain proteins from their sols, but left the question of the size of particles open. Filtration through gels was eventually developed by H. Bechhold into a fairly simple procedure, with only moderate pressures—rarely more than five atmospheres—and called by him, in allusion to the

ultra-microscope "Ultra-Filtration." Membranes similar in nature to those used in dialysis are employed, but the outside is not submerged in the solvent. To permit the use of pressure, the membranes are prepared as follows: strong, hard filter paper is impregnated, preferably *in vacuo*, with either a gelatin sol or acetic acid collodion of known concentration. The gelatin filters are then immersed in cold formaldehyde for several days and rendered insoluble, while the collodion filters are immersed in water, which gradually replaces the acetic acid and leaves a gelatinous mass of nitro-cellulose in the substance of the paper. The filters are clamped in a small pressure vessel and are supported on wire gauze and perforated metal, so that pressures up to 10 atmospheres can be used, if necessary. A very important feature, predicted and subsequently verified by Bechhold, is the ease with which the porosity of these filters can be varied by altering the concentration of the original gelatin or collodion, so that particles which pass freely through a "2·5 per cent." collodion filter, *i.e.*, one made from a collodion containing 2·5 gm. of nitro-cellulose in 100 c.c., can be completely retained by one made from 5 per cent. collodion.

The size of the pores in these septa, which interests us at the moment, can be determined by two methods indicated by Bechhold; either by ascertaining the pressure required to force air through a membrane saturated with water, or by measuring the volume of water forced through unit area in unit time by a known pressure. Both calculations involve a considerable number of simplifying assumptions, and a very high degree of accuracy cannot be expected from them, though there is no doubt about the results being of the correct order. A third method was indicated by the author, and consists in determining the pressure at which oil globules of known

size, suspended in water, are just forced through the membrane. If the interfacial tension oil-water is known, the radius of the pores—assumed to be of circular section—can be calculated with a fairly high degree of accuracy.

The result of Bechhold's determinations is that, according to the concentration of the collodion or gelatin used, the diameters of the pores lie between 930 $\mu\mu$ and 21 $\mu\mu$ (the $\mu\mu$, which is the unit generally employed in giving the dimensions of such particles as we shall have to deal with, is 0·001 μ, and therefore one-millionth millimetre, *i.e.*, 1×10^{-6} mm. $= 1 \times 10^{-7}$ cm.). These dimensions give us *limits* for the sizes of the particles retained by such filters; if the particles are retained, they are probably, though not necessarily, larger than the pores; if they pass through the filter, it is reasonably certain that they are much smaller than the pores.

Evidence tending in the same direction and towards the same limits is afforded by an optical property of many sols. Although the latter may be perfectly clear in transmitted light, the path of an intense beam of light projected through them and viewed, best against a dark background, at right angles to its direction, becomes clearly visible, the liquid appearing either more or less turbid, while sometimes exhibiting a different colour from that shown in transmitted light. The phenomenon was noticed already by Faraday in his gold sols; it was subsequently employed by Tyndall in the study of fogs, etc., and is generally called the Tyndall cone. If the cone is viewed through some suitable analyzer, it is found to be polarized, and it must be emphasized that herein lies its difference from true fluorescence; the blue cone seen under similar conditions of illumination in a solution of quinine sulphate, or in certain petroleums, is not polarized. The whole phenomenon has been investigated mathematically by Lord Rayleigh,

who proved that to produce it, the particles in the path of the beam must be small compared with the wave-length of light. The values of the latter are, of course, known with very great accuracy, and lie between 450 and 760 $\mu\mu$ for the visible spectrum. These limits, again, agree well with those deduced from the study of ultra-filters.

At the same time, they answer a question which may already have occurred to the reader: why the size, or at least the presence of such particles as may be present in a sol, cannot be ascertained directly by microscopic observation? The answer is, that objects small in comparison with the wave-length of light are invisible in the ordinary microscope. The limit of resolving power of the best microscope is $0{\cdot}2\ \mu = 200\ \mu\mu$, which does not, however, mean that particles of this, or larger size, can necessarily be made visible.

It has, however, been known for some time that with favourably arranged illumination objects even of submicroscopic dimensions could be rendered visible. Thus it had been shown by Fizeau and by Ambronn that slits of much smaller width than the limit of resolution could be seen if strongly illuminated on a dark ground. These observations suggested to Zsigmondy and Siedentopf the possibility of rendering visible the individual particles which collectively produce the Tyndall phenomenon, if only the light scattered by the particles (reflection in the ordinary sense cannot take place from objects smaller than the wave-length of light) was permitted to enter the microscope, but no direct rays from the source of light.

This expectation has been fully realized and the "ultra-microscope" has now become a familiar and indispensable instrument of research. The name may be misleading, unless it is remembered that the microscope used is of the ordinary kind, and that

only the method of illuminating the object is different. The principle of the latter is very simple ; a powerful beam of light is thrown horizontally through a small body of liquid, and the illuminated volume is observed through a microscope, the axis of which is vertical. It is at once obvious that no light enters the instrument except such as has been scattered by particles present in, *and optically different from*, the liquid itself, *i.e.*, they must be opaque or possess a refractive index different from that of the latter.

Any particles present under these conditions appear as light discs on a dark background. The images are not geometrical images, and their apparent size is not increased by the use of higher powers. The effect of the latter is merely increased magnification of the distances between particles and of any motion which they may possess. The visibility depends on the intrinsic brilliancy of the source of light and on the optical difference between the phases ; if the latter is great, particles as small as 5 $\mu\mu$ diameter can still be distinguished with direct sunlight. In many sols, however, particularly organic ones, no particles can be seen even in the most favourable conditions, but only a diffuse light. This may be due to their small size, but the other possibility, an insufficient optical difference between disperse phase and dispersion medium, must not be overlooked. We shall see that in many cases the disperse phases must be considered to contain considerable amounts of solvent in some way associated with their substance, and the optical difference may thus become very small, while the particles are likely to be comparatively large.

Since the images, as has already been explained, are not geometrical, *i.e.*, bear no known ratio to the size of the object, direct measurements are still impossible. The size of particles seen in the ultra-microscope can however be calculated by an indirect

method, which will be more easily understood after a short description of the instrument as actually used. This is shown in Fig. 1. The light of a large arc lamp *d* is projected by the lens *f* on a "precision" slit *g*, the width and height of which can be adjusted very accurately, and which can be rotated round an horizontal axis. An image of the slit is formed by the second lens *h* and projected on the illuminating

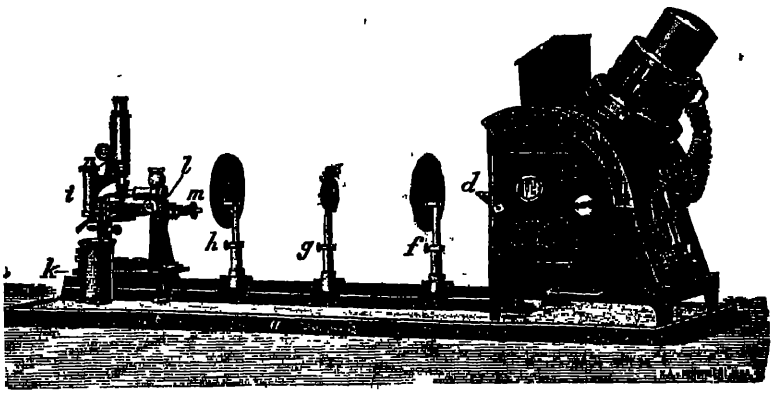


FIG. 1.—GENERAL ARRANGEMENT OF THE SLIT ULTRA-MICROSCOPE.

device proper *l*, which is substantially a microscope objective. This throws an intense beam of light through a cell containing the liquid to be examined, which is seen more distinctly in Fig. 2, where it is shown in position on the microscope. It is of rectangular cross-section and has two windows—the one in front admits the beam of light, while the second is at the top opposite the objective of the microscope. The cell is provided with a funnel at one end and an outlet at the other, so that a large volume of liquid can be passed through and examined at one setting.

A small portion of the illuminated volume can be delimited and the length—in the direction of the axis

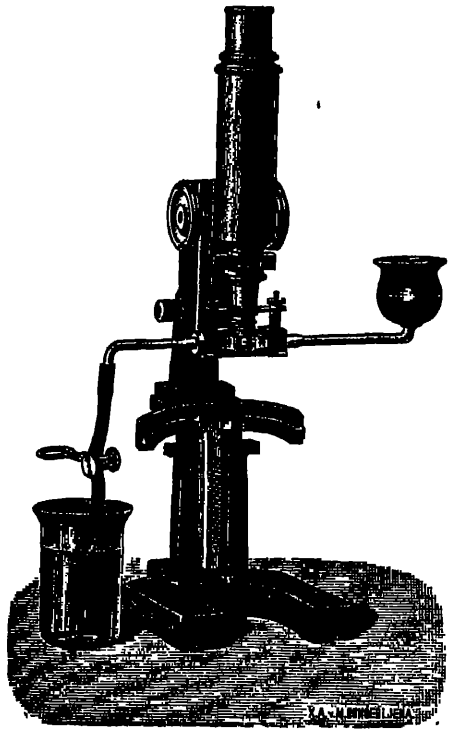


FIG. 2.—MICROSCOPE WITH QUARTZ CHAMBER FOR ULTRA-MICROSCOPIC EXAMINATION OF LIQUIDS.

of the beam—as well as the width measured directly by means of an eye-piece micrometer; the depth is determined by turning the slit 90° so that what was the depth of the illuminated prism can now also be measured. The sol is diluted so far that only a

small number of particles are visible in this known volume, and their average number is determined by repeated counts. The *weight* of disperse phase in unit volume is known from its method of preparation, and the weight present in the observed volume, which is, of course, of the order of cubic μ, is calculated therefrom. Dividing this weight by the number of particles observed, we obtain the weight of one particle, and we can then calculate its dimensions by making two assumptions: 1. That the density of the particles is the same as that of the material in bulk; and 2. That the particles have a simple geometrical shape, *e.g.*, spherical or cubical. In the generality of cases probably neither assumption is correct, but there is no doubt about the order of magnitude thus calculated being right. Very many determinations of this kind have been made by numerous observers, since the invention of the ultra-microscope, and we shall have occasion to refer to them again.

Particles visible in the ordinary microscope are generally described as microns, those which can be made visible by the ultra-microscope as submicrons, and those which cannot be rendered visible even by the latter, as amicrons. As has already been pointed out, however, these differences are not determined by the size alone.

The apparatus described is the most perfect one for the observation of ultra-microscopic particles, and the only one which can be used for determining their size. As it is rather costly and requires powerful illumination, a number of devices have been introduced with which the ordinary axial illumination can be employed, while direct light—other than that scattered by particles—is still prevented from entering the microscope. In a number of them this object is effected by total reflection from the cover glass; the principle will be

readily understood by reference to Fig. 3, which shows a section of the "paraboloid" condenser made by Carl Zeiss. The condenser is part of a paraboloid of revolution, bounded by two parallel planes at right angles to the axis. Parallel rays entering the condenser axially are, as is well known, reflected into the focus of the paraboloid, and the top face of the condenser is so adjusted that this focus falls on the surface of the slide, which is of a definite thickness.

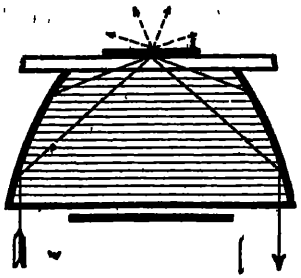


FIG. 3.—SECTION OF PARABOLOID CONDENSER, SHOWING PATH OF RAYS.

A central stop covers part of the bottom face and permits only such rays to pass as will, after reflection, strike the surface under an angle greater than the critical angle, so that they would be totally reflected by the top of the condenser if in contact with air. By placing cedar oil between this surface and the slide, the light is enabled to pass through the latter and any liquid placed on it for examination, but is totally reflected at the cover glass which rests on this liquid. The field therefore is dark if the liquid is quite free from particles, while, if they are present, the light scattered from them—as indicated by the dotted lines—can enter the microscope and form an image.

The use of slides and cover glasses involves several disadvantages; these are avoided by the design illustrated in Fig. 4, which represents a section through the Jentzsch "ultra-condenser." The liquid is placed directly in the spherical hollow *a*, which is closed by a quartz cover (not shown), and holds about 1 c.c. The lower face of the condenser is

provided with a central stop. The rays which enter are twice reflected as shown by the dotted lines, and come to a focus in the axis at some point near the top of the cavity *a*. A thin layer of the liquid is thus illuminated very intensely, while no direct light passes axially. The particles visible are observed at some distance from any glass surface, which eliminates various disturbing factors. A small hand-regulated arc must be used as source of light, while a large incandescent gas burner, or a "Point o' light" lamp, is sufficient for the slide and cover-glass types.

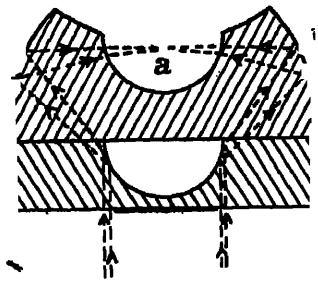


FIG. 4.—SECTION OF ULTRA-CONDENSER, SHOWING PATH OF RAYS.

All these appliances can be fitted to ordinary microscopes and permit a rapid diagnosis, though only the "ultra-condenser" approaches the slit ultra-microscope when very small particles are to be rendered visible.

The result of our brief and general survey of the various methods for examining colloidal solutions is that the majority contain the disperse phase as particles below the limit of microscopic visibility, but capable of being rendered visible and measured, as well as capable of being retained by certain porous septa. The sizes at which we arrive by these methods are still, even in the cases of the smallest submicrons, considerably larger than the limit values for the size of various molecules deduced by numerous investigators employing a great variety of methods.

In this presence of particles of sizes greatly exceeding molecular dimensions must be sought one of the fundamental differences between colloidal and

true solutions. While this characteristic, or rather the order of magnitude, alone would explain certain properties of sols, such as their extremely low osmotic pressure, it fails, by itself, to account for others and more especially for those in which various sols differ very strikingly from one another. We shall discuss these differences and the way in which they lead to a classification of sols in the next chapter.

CHAPTER III.

A PROPERTY which varies very markedly in different sols is their behaviour to electrolytes. The metal and sulphide sols, or the copper ferrocyanide sol described on p. 11, show an immediate change on the addition of electrolytes even in small concentrations; they either change colour or become turbid, and after a certain time the whole of the disperse phase settles out, leaving the supernatant dispersion medium clear. An addition of, say, 1 c.c. of normal sodium chloride solution to 19 c.c. of the copper ferrocyanide sol will produce these changes within a few minutes. On the other hand, the addition of this amount of sodium chloride solution to the albumin sol will not produce any obvious change at all, and even very much greater quantities will fail to do so. Other sols, while still extremely sensitive to electrolytes, undergo a different kind of change; the disperse phase is not separated as precipitate, but the whole liquid sets to a coherent gel. Silicic acid sol and ceric hydroxide sol are examples of this type, the latter a particularly striking one.

This difference in the behaviour towards electrolytes has been made the basis of a classification by Perrin and by Freundlich, who divide colloids into "lyophobe" and "lyophile," *i.e.*, such as remain reluctantly, and such as remain freely in solution, in presence of electrolytes. While this is no doubt an important criterion, the distinction is purely descriptive, and we shall endeavour to find a classification which goes more directly to the root of the matter, *viz.*, that first proposed by Wolfgang Ostwald.

This takes as its basis the state of aggregation of the phases, in other words it looks on colloidal solutions as special cases of the disperse system. The dispersion medium in the types of immediate interest to us is liquid, so that the classification rests on the state of aggregation of the disperse phase, which may be solid, liquid or—though this hardly concerns us—gaseous.

We could probably predict some properties of systems having particles within the colloidal range of sizes and either solid or liquid, but it is both easier and more convincing to proceed by way of analogy from coarser systems. One property which exhibits very marked differences in different types of sols, and does so equally in coarse systems composed of known phases, is the viscosity, and we will consider these differences in some detail.

The reader is no doubt aware of what is understood, in a general way, by the viscosity of a liquid: the resistance offered to shearing, stirring or the flow through a capillary tube. If a liquid is contained between two parallel plates and one of them is moved with constant velocity in its own plane, a certain force is required to maintain this velocity, which depends on the latter, the area and distance of the plates and on the nature and temperature of the liquid. This gives us the definition of the *viscosity coefficient, at any given temperature*: the force required to move a plate of unit surface separated from a plate of the same size by a layer of liquid of unit thickness, at unit velocity. Such coefficients for many liquids, expressed in absolute units, can be found in the various tables of physical constants. They all decrease rapidly with rising temperature, the decrease in many cases amounting to several per cent. per degree C.

The viscosity cannot be conveniently measured by any method directly embodying the definition,

but the coefficient can be deduced from the time of flow through a capillary under known conditions. The text-books of physics should be consulted for the theory and details of the method and for the various criteria to be satisfied if the measurements are to be correct.

As regards colloidal solutions, they fall very distinctly into two classes in respect of the increase in viscosity over that of the pure dispersion medium, produced by a given percentage of disperse phase. One class, the metal and sulphide sols in particular, shows a viscosity only very slightly higher than that of water. The other, which comprises principally the organic colloids, such as albumin, gelatin, agar, etc., shows a very considerable increase of viscosity, even with small percentages of dissolved matter. Even more striking is the increase caused by certain colloids in organic dispersion media; rubber sols containing 1 per cent. of rubber in benzene may have a viscosity 60 to 100 times that of pure benzene, while sols of nitro-cellulose of the same concentration may have viscosities several hundred times greater than the dispersion medium.

Coarse systems show very similar differences. It is a fact familiar to everybody who has stirred up finely divided *solid* matter, such as precipitates of calcium carbonate or of barium sulphate, with water, that even with 20 or 30 per cent. the mixture does not offer any great resistance to stirring, *i.e.*, the viscosity is not much increased. On the other hand, it is equally well known that systems of two liquid phases insoluble in each other, generally called emulsions, show a viscosity much higher than that of either phase, though it is not realized how great this increase may become. Various pharmaceutical and domestic preparations are familiar to everybody; a good example of the latter is mayonnaise sauce, an emulsion of oil in yolk of egg. The viscosity

increases steeply with increasing percentage of disperse phase, extreme cases being represented by certain emulsions used as " solid " lubricants, and by Pickering's emulsions with 99 per cent. of mineral oil in 1 per cent. of soap solution, which could be cut into cubes.

Applying these considerations to sols, we are led to the conclusion—now fairly generally accepted—that in those which show a low viscosity the disperse phase is present as solid particles, while in the sols with high viscosity the disperse phase is liquid. The distinction between solid and liquid involves some difficulties when applied to ultra-microscopic bodies, which will be referred to again; as, however, the particles must consist of a number of molecules, it is obviously possible that in one case they may be held together by the forces characteristic of the solid state, while in the other the cohesion may be of the same kind as in liquids, *viz.*, accompanied by relative mobility, although we shall find this restricted by the action of the surface. That the former assumption is correct, at least in one typical case, has been proved by Debye and Scherrer (*Phys. Zeitschr.*, *17*, 277, 1916) by X-ray analysis of the particles of protected gold sols. They invented a method for applying this to arbitrarily orientated particles and found the space lattice of the ultra-microscopic particles to be exactly the same as that of large gold crystals, a result which leaves no doubt regarding the state of aggregation.

No such direct demonstration is possible in the other class of sols, and the first difficulty is that the disperse substance in its original state, such as dry albumin or dry nitro-cellulose, is not liquid. We have, therefore, to make a further assumption: that the substance, in being dispersed, becomes associated with considerable amounts of the dispersion medium, and that these highly hydrated (or,

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in media other than water, "solvated" aggregates constitute the disperse phase and possess the free deformability of the liquid state. This conception is not an easy one, but it rests fortunately on other evidence as well as the mere analogy in viscosity. The latter is not only high, but exhibits anomalies that distinguish it sharply from that of homogeneous liquids with very high viscosity, such as glycerin or castor oil. The viscosity of most sols of this class is not a real constant for a given temperature; it may decrease (ceric hydroxide sol) or increase (gelatine, silicic acid sol) merely with age. By appropriate methods it can further be shown, that at any given time the viscosity is not, as with homogeneous liquids, independent of the *rate* at which the liquid is sheared, but varies enormously with this rate. This anomaly was first investigated by H. Garrett (Dissertation, Heidelberg, 1903), and many measurements revealing it have been carried out by the author (*Koll.-Zeitschr.*, *13*, 88, 1913). Even somewhat prolonged shearing at the same rate may alter the viscosity markedly. A further factor to be considered is the decrease in viscosity with rising temperature. As we have already mentioned, all liquids show this decrease, but if we compare the temperature coefficient of the viscosity of, say, a gelatine sol with that of the dispersion medium, water, we find the former enormously greater. This fact is probably most easily and naturally explained by a change in the degree of hydration, which involves a transfer of water from one phase to the other.

Further and more direct evidence of the state of aggregation of the disperse phase is furnished by the fact that some sols of the class we are describing, such as gelatin or soap sols, can, by the addition of neutral salts, be separated into two *liquid* layers, both of which contain the dispersed substance, but in very different concentrations. An experiment by

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W. Pauli and P. Rona shows this very convincingly: a 10 per cent. gelatin sol receives an addition of sodium sulphate at 30° C., which produces a copious coagulum. On allowing the preparation to stand for several hours at the same temperature, it will be found that the coagulum has completely coalesced to a *liquid* layer of concentrated gelatin, which is separated by a sharp boundary from a supernatant layer of dilute gelatin sol. Since it is certain—from the analogous effect of salts on, say, a mixture of alcohol and water—that the first effect of the salt is a withdrawal of water, and since the portion of the system from which the water has been removed proves still to be liquid, it is only reasonable to infer that it was liquid when it contained more water, viz., in its initial condition.

Disperse systems with liquid dispersion medium and solid disperse phase are known as suspensions, while those with liquid dispersion medium and liquid disperse phase are called emulsions (see p. 8).

Wolfgang Ostwald accordingly calls the sols with solid disperse phase "*Suspensoids*," and those with liquid disperse phase "*Emulsoids*," which terminology will be used throughout this book. The two classes coincide to some extent, though by no means completely, with the "lyophobe" and "lyophile" colloids respectively.

The suspensoids show a much more uniform behaviour towards various influences than the emulsoids, and will, therefore, be considered first. We are now in the possession of two data: we know the approximate size of the particles, and we have concluded that they are solid. The next step is to co-ordinate these two factors by examining the behaviour of small particles suspended in a liquid, and especially to study how this behaviour changes when their size decreases to ultra-microscopic dimensions.

CHAPTER IV.

It was shown by Stokes in 1850 that a *small* sphere falling in a liquid soon assumes a constant velocity, which is given by a formula that has since played a part in an enormous number of most important investigations. The formula applies strictly only when the liquid is infinitely extended and corrections have to be made if the sphere falls in the vicinity of a wall or in a narrow vessel. If we call :—

r the radius of the particle,
s the specific gravity of the same,
s' the specific gravity of the liquid,
η the viscosity of the latter,
g the gravity constant,

the constant velocity of the particle is :—

$$V = \frac{2r^2(s - s')g}{9\eta}$$

It is obvious that the difference $(s - s')$ may be positive, zero or negative—that is, the particle may sink, remain stationary or rise, if its specific gravity is greater, equal to, or smaller than that of the liquid. It is also obvious that, other things being equal, the velocity, in whichever direction, is inversely proportional to the viscosity of the liquid.: a particle of given size and weight will sink several hundred times faster in water than in castor oil. The point which, in the present connection, interests us most is that the velocity, other things being equal, is proportional to the square of the radius.

To fix ideas it will be useful to consider an example in figures, say a gold particle of 1 μ radius or 2 μ

diameter. Introducing the proper values (all centimetres, grammes and seconds), viz., $r = 10^-$ $s = 19{\cdot}3$, s' (water) $= 1$, $g = 980$, η at 20° C. $= 0{\cdot}0$ we find the velocity of the particle about 0·04 mr per second, or 2·4 mm. per minute.

This is a considerable speed and means, in oth words, that such a suspension of gold particles wou clear at the rate of 2·4 mm. per minute from the to and would be clear to a depth of about 14 cm. at tl end of one hour.

Assuming now the radius to be 1/100 of that ju considered, or 10 $\mu\mu$, which is the size of the particl in many red gold sols, the velocity would be 1/10,0(of that calculated. This makes it only 0·014 mr per hour, or about 10 mm. *in one month.* Wi particles of lower specific gravity the rate of settlir would be proportionately slower: with a speci gravity of 3, instead of 19·3, it would be about on sixth of the above figure, *i.e.*, about 1·3 mm. p month.

This little calculation shows us that, with particl of ultra-microscopic size, a suspension may appe very stable and may take a very long time to sho marked clearing or sedimentation. At the san time, disperse systems with ultra-microscop particles differ from coarser ones in their liabilit already referred to, to undergo irreversible transfo mations. A coarse suspension is *reversible*: whe it has settled, however long the process may take, can be restored to its original condition by me shaking or agitation, and this may be repeate indefinitely. This is not generally possible with so like the metal sols; when these have coagulated, tl gel can hardly ever be transformed back into tl original sol merely by mechanical agitation. We a therefore forced to the conclusion that the particl are subject to other influences besides those of gravi and of viscosity, and investigation shows th

reasoning to be correct, inasmuch as the particles are in violent motion, and are also electrically charged.

The motion of the particles is the most striking feature of the ultra-microscopic picture. It is, however, visible even with much larger particles and ordinary illumination, and was first observed (on pollen grains suspended in liquid) by Dr. Robert Brown, the botanist, after whom it is called the *Brownian movement*. The movement is composed of an oscillating motion of the particles round a central position, and an erratic translatory motion. Description is rather inadequate, but, if an ultra-microscope or ultra-condenser is not available, it may be seen quite well in a suspension of gamboge (the ordinary water colour) with a magnification of about 500 diameters and such simple dark ground illumination as can be obtained with a central stop in the Abbe or achromatic condenser.

The phenomenon received attention from a number of investigators, including Wiener, Gouy, Jevons Exner and Ramsay, during the nineteenth century. It was shown that particles of any material showed the movement, provided they were sufficiently small, that it decreased with increasing size and became imperceptible when the size increased above about 3 μ diameter. Various suggested causes, such as vibration, convection currents due to changes of temperature or concentration, the effect of illumination, etc., were gradually eliminated by experiment, and towards the end of the century the opinion gained ground that the cause of the movement had to be sought in some factor inherent in the liquid state. The invention of the ultra-microscope gave a great impetus to the study of the phenomenon, as the very small particles revealed by it for the first time showed such a vivid motion that Zsigmondy was inclined to look on it as something differing not only in degree, but also in its nature from the Brownian movement as known up to then.

Quantitative relations were first established in 1906, both by experimental investigation and by mathematical treatment. The former was carried out by Svedberg, who allowed sols to flow through the chamber of the ultra-microscope with the effect that the Brownian movement was combined with the translatory motion of the liquid as a whole, the path of the particle appearing as a wave line. Relations could then be established between the amplitude and the wave-length, both being measured by the eye-piece micrometer. The former is the maximum deviation—more correctly its projection on a plane perpendicular to the axis of the microscope—of the particle from a mean position, while from the wave-length and the known velocity of flow through the field the period, *i.e.*, the time taken by the particle to return to the mean position, could be deduced. From a great number of observations on sols with different disperse phases and different dispersion media Svedberg deduced two relations: (1) For a given radius the amplitude is inversely proportional to the viscosity of the dispersion medium; and (2) The period is proportional to the amplitude. In symbols these relations may be written :—

$$(1) \quad A\eta = C_1 \qquad (2) \quad A/P = C_2$$

where A = amplitude, P = period, η = viscosity and C_1 and C_2 are constants.

In 1906 the problem was treated mathematically by Einstein and by v. Smoluchowski on the assumption that the movement was caused by the impact of the molecules of the dispersion medium on the particles. Their results, although obtained by different methods, are identical except for a numerical constant. Smoluchowski's formula is :—

$$4A^2 = \frac{64}{27} \frac{P}{2} \frac{RT}{3N\pi\eta r}$$

in which A, P and η have the same meaning as above;

r is the radius of the particle, while R is the gas constant, T the absolute temperature and N Avogadro's number. Einstein's formula has the factor 1 instead of 64/27.

For a given radius r and temperature T the expression on the right hand becomes constant with the exception of η and P, and by a simple transformation we can write it :—

$$4A^2\eta/P = C_3.$$

It will readily be seen that the same result is obtained by multiplying the two expressions found experimentally by Svedberg with each other.

The question is sometimes asked why the impacts of the liquid molecules do not balance each other, *i.e.*, why they produce any visible movement at all. The answer is, of course, that, when the particles are small, the probability of the impacts exactly balancing in a given short time is also small ; it increases with increasing size, with which the Brownian movement finally becomes imperceptible.

Einstein's and v. Smoluchowski's deductions lead to a view which has been very clearly put by Perrin ; that disperse particles differ from molecules merely by their size or, in other words, may be looked upon as very large molecules. This leads to several consequences that can be tested experimentally ; one of them is *that the particles in a disperse system must, under the influence of gravity, arrange themselves as do the molecules of a gas in the same conditions.* It is well known that the density of a gas, *i.e.*, the number of molecules in unit volume, varies with the height according to an exponential law, and a similar law should therefore hold good for the number of particles at different heights in a disperse system. While, however, it is necessary to ascend to considerable heights in the atmosphere to show a marked decrease in density (*i.e.*, pressure), a

difference in concentration should be demonstrable at very slight differences of level when the molecules are of enormous size. Perrin examined suspensions of gamboge particles of uniform size, and counted the particles at different levels in a layer of only 0·12 mm. total thickness. He found that the number actually decreased with increasing height according to an exponential law. The "molecular weight" of the gamboge particles was found to be about 3×10^9.

For further details of these classical researches the reader is referred to Perrin's work, which has been translated into English by Soddy under the title, "Brownian Movement and Molecular Reality."

We will mention only one further result of these investigations; they may be used for calculating Avogadro's number, *i.e.*, the number of molecules contained in 1 gramme-molecule of any gas. The value found by Perrin, 7×10^{23}, agrees well with the values found by a number of methods based on entirely different principles.

The view that suspensoid particles may be considered as very large molecules leads to one or two further conclusions, which are in complete accordance with experience. Owing to the high "molecular weight" and the—generally—low percentage concentration, the *molecular* concentration of suspensoid sols is extraordinarily small, and we should, therefore, not expect them to show appreciable osmotic pressures. For similar reasons we must expect very low diffusion constants; both conclusions are borne out by experiment. At the same time it is obvious that, as the size of the disperse particles decreases there must be a steady increase in osmotic pressure, for a given amount of disperse phase, and a steady transition to molecular or "true" solutions—even though every step of this transition may not be capable of experimental realization.

It is evident that the Brownian movement, especially with particles of ultra-microscopic size, is a factor which counteracts sedimentation. As it is not confined to this range, but occurs with particles that separate, it is, however, not the only one, since it is not affected directly by factors which destroy the stability of suspensoid sols, *e.g.*, the addition to them of electrolytes. A second factor intimately connected with the stability of sols on the one hand, and the *irreversible* character of the transformations they undergo on the other, is the electric charge on the particles.

Although the electrical properties of the suspensoids have probably received more attention than all others together, the origin of the electric charge is still a subject of controversy, which will be more conveniently discussed when we have become familiar with the preparation and properties of individual sols. Here it may be said that any substance in contact with water and many other liquids assumes an electric charge, which can be varied both in amount and *in sign* by the addition of electrolytes, and may become zero at suitable concentrations of the latter. In this condition, as has been shown by Hardy and by Burton, suspensoid sols are particularly unstable and tend to precipitate; the electrolyte concentration at which the disperse phase shows no charge has been called by Hardy the *isoelectric point*. Anomalies, viz., maximum instability when the particles are not electrically neutral, have been observed and will be referred to again.

However obscure the origin of the charge, its existence, and that of the opposite charge on the dispersion medium, can easily be demonstrated. If an electric field is produced in a disperse system, whichever phase can move freely will move towards the electrode having the opposite sign to that carried by the moving phase. Thus, in a sol the particles will travel, while, if we fix the disperse phase, say,

in the shape of a porous plug in a tube filled
water, the liquid will flow. The latter phenome

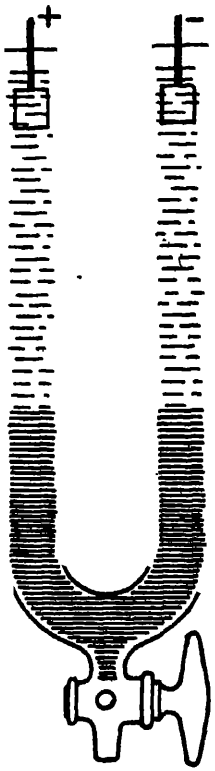


Fig. 5. — U-Tube for Cataphoresis.

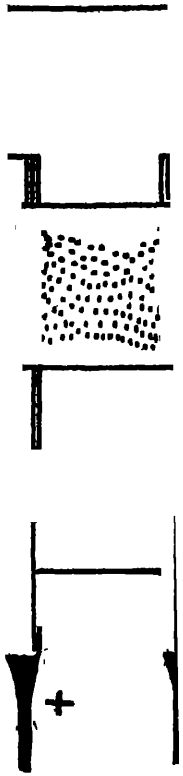


Fig. 6. — Slide Microscopic M
surement of C.
phoresis.

which is of technical interest, is called *elec.*
endosmosis; the former, which is employed to det
mine the sign of the charge on suspensoid partic

is generally called *cataphoresis*, although electrophoresis would be a more suitable general term.

Cataphoresis can be demonstrated by macroscopic as well as by microscopic methods. The former consists, in principle, in placing the sol to be examined into the bend of a U-tube (Fig. 5) and filling the limbs with pure water or, more correctly, with some liquid which does not give rise to a difference of potential at the surface of contact with the sol. Electrodes dip into the limbs and, when these are connected to a source of current, the particles gradually wander into the water surrounding the pole of opposite sign, so that negatively charged particles travel to the *anode*, and positively charged particles to the *cathode*.

The microscopic method was first used by Cotton and Mouton and permits the use of very small volumes of liquid. An ordinary microscope slide (Fig. 6) is provided with a pair of parallel electrodes of platinum foil, which are connected by suitable leads to a couple of cells or accumulators. A drop of the liquid under examination is spread on the slide so as to be in contact with both electrodes and covered with a cover glass. The preparation is illuminated with one of the dark-ground condensers previously described and examined under the microscope, when the particles will be seen to travel towards either electrode.

In the U-tube it will be noticed that the boundary between sol and clear water advances parallel to itself towards the electrode, which shows that all particles travel with the same speed. If disturbing factors are avoided, the same observation is made by the microscopic method. This speed does not differ widely even in different sols, and lies, generally speaking, between 1 and 4×10^{-4} cm./sec. in a potential gradient of 1 volt/cm. These values do not differ greatly from the velocities of the slower ions.

CHAPTER V.

IN the preceding chapter we have defined the suspensoids as systems containing the disperse phase as solid particles below a certain size, in constant movement and electrically charged. We shall now consider a number of typical representatives of the class in some detail and incidentally attempt to classify the methods by which suspensoid sols—all of which are laboratory products—are obtained.

Since we have to obtain the disperse phase in particles of a size lying between definite limits, we can obviously reach the desired degree of dispersity from either side, at any rate in principle, *i.e.*, we may start from ions and molecules, or we may start from material in a coarser state of division and comminute it to the desired extent. This distinction was first drawn by Svedberg, who divides the methods for producing sols into *condensation* and *dispersion methods*. The former include practically all methods which employ a chemical reaction for producing the disperse phase.

The sols of the noble metals, and more especially of gold, are among the most typical examples of the latter procedure, and have been studied exhaustively. To prepare gold sol, a very dilute solution of either $AuCl_3$ or $HAuCl_4$, containing 1 part in 10,000 or frequently less, and either exactly neutralized or made slightly alkaline, is reduced by one of a large number of reducing agents, either at ordinary temperature or at boiling point. Among reducing agents which act in the cold are hydrazine, phenylhydrazine, hydroquinone, pyrocatechin, pyrogallol,

etc., the resulting sols being blue or purple. Reducing agents which are used in hot solution include ethyl alcohol, formaldehyde, tannin, dextrin, etc. With suitable procedure and precautions, for which the works on practical colloidal chemistry must be consulted, these produce beautiful ruby red sols without any purple tinge. All these are stable, but some of them, particularly the sols reduced by ethyl alcohol or by formaldehyde, are so sensitive to low concentrations of foreign electrolytes, that even the small quantities of glass dissolved from ordinary glass ware, or acid from the laboratory atmosphere, cause a change, so that they must be kept in well-stoppered vessels of resistance glass.

Silver sols may be obtained in similar fashion by reducing very dilute solutions of silver nitrate, made alkaline with ammonia or sodium hydroxide, with most of the organic reducing agents mentioned above in the cold. They show a great variety of colour, from blue (hydroquinone) to light brown with a marked greenish tinge in reflected light (tannin). Of great interest are the silver sols first prepared by Carey Lea, especially on account of the very high concentration of disperse phase. He reduced silver nitrate with mixtures of ferrous sulphate and an alkaline citrate or tartrate, or else with dextrine in the presence of caustic alkali. Blue or brown precipitates result, which, after washing with dilute salt solutions or with alcohol disperse spontaneously in water to form sols with concentrations of 10 per cent. and more.

A method of producing silver sols which possesses considerable theoretical interest is the reduction of solutions of silver oxide by gaseous hydrogen, which has been exhaustively studied by Kohlschütter. Hydrogen is bubbled through a saturated silver oxide solution, containing some oxide in excess and maintained at the optimum temperature of 55° to

60° C. A yellow sol is gradually produced, which still contains silver oxide as well as metallic silver. Kohlschütter found that the reduction took place exclusively at the wall of the vessel and that the material of the latter exerted a considerable influence on the colour of the sol. In platinum vessels no colloidal silver is formed at all, but the reduced metal appears in shining crystals on the platinum surface. The oxide still remaining in a sol prepared in a glass vessel can therefore be removed by continuing the treatment with hydrogen in platinum vessels. The interest of the method lies in the possibility of producing a sol practically free from electrolytes, while it will be readily understood that the methods described so far, and to be still mentioned, all leave electrolytes resulting from the reaction in the sol.

Sols of the metals of the platinum group can also be obtained by direct reduction with hydrazine, etc., but are rarely stable without certain additions which will be discussed later. Sols of mercury appear to have been made for the first time by Lottermoser, who reduced solutions of mercurous nitrate with stannous nitrate.

As regards non-metallic elements, tellurium and selenium sols can be obtained by reducing solutions of the dioxides with hydrazine or phenylhydrazine hydrochloride. The latter sol is a vivid red. The most extensively studied sol, however, is that of sulphur: the work of early investigators has been mentioned in Chapter I. An important modern method of preparing colloidal sulphur is that of Raffo: the decomposition of sodium thiosulphate by concentrated sulphuric acid. Some of the sulphur liberated by the reaction is coarse, but a large fraction is colloidal, and can be separated and purified by suitable treatment. This method has been developed by Sven Oden, who has made colloidal sulphur the

subject of probably the most exhaustive study devoted to a single sol (*Der kolloide Schwefel*, Upsala, 1913).

Among the numerous compounds which can be obtained in the suspensoid state the sulphides must be particularly mentioned. Arsenic trisulphide, which is easily obtained—as noticed already by Berzelius—by passing hydrogen sulphide into a solution of arsenious oxide, has been the subject of the classical investigations of Linder and Picton. Mercuric sulphide can be obtained, in either water or alcohol as dispersion medium, by passing hydrogen sulphide into a solution of mercuric cyanide.

Other compounds can be referred to only very briefly. Of great theoretical interest are Lottermoser's investigations on silver haloid sols. These can be obtained by double decomposition in suitable concentrations if either the Ag ion or the halogen ion is kept in excess throughout the reaction, *i.e.*, by pouring a certain volume of dilute $AgNO_3$ solution into a somewhat larger volume of an *equivalent* solution of KI or KBr, or *vice versâ*. An important difference between the sols resulting from these converse procedures will be discussed later on.

The condensation methods, of which a few examples only have been described, have certain features in common. The disperse phase is produced from—generally speaking—very dilute solutions of the reaction components, and in practically all cases electrolytes, in correspondingly low concentrations, are present in the sol. That these play some part beyond that of unavoidable by-products is proved by the observation, which can be made with most sols, that attempts to remove the electrolytes completely by dialysis lead to the coagulation of the sol. The probable cause of this behaviour will be conveniently discussed in connection with the electrical properties.

The mechanism of the condensation methods has been completely elucidated by the labours of P. P. von Weimarn. Without going into detail or reproducing the mathematical formulation it may be said briefly that he treats suspensoid formation as a special case of crystallization from supersaturated solution. If we produce an insoluble or, strictly speaking, very slightly soluble substance, it will separate in particles which, according to v. Weimarn, are always crystalline whatever their size. If we wish to keep the latter within certain limits, two conditions have to be satisfied; condensation must begin in a large number of places, and the growth of the nuclei thus formed, which necessarily will be of molecular dimensions at first, beyond the desired limit must be prevented. Provided a disperse system is to form at all, more reaction product must be formed than can exist in *true solution* in the particular dispersion medium used; the ratio of this excess/solubility settles the rate of condensation, which varies in the same sense as the ratio. It can, therefore, be increased in either of two ways—by increasing the excess or by reducing the solubility. If the latter is appreciable (the solubility of barium sulphate, 0·00024 gm. in 100 c.c. at 18° is appreciable in the present connection) the excess must be large; in that case, while the precipitate is still highly disperse, the particles are so numerous and close together that a gel is formed. If the excess is smaller, the solubility must be reduced; in the case of barium sulphate this can be accomplished, *e.g.*, by adding alcohol to the reaction mixture, when a stable sol of barium sulphate can be obtained. The growth of the nuclei again depends on the amount present in true solution, *i.e.*, on the solubility and on the rate of diffusion; the latter depends on various factors, including the viscosity of the dispersion medium. By a suitable adjustment of these

variables, practically any substance may be made to form a sol; v. Weimarn and his school have proved this possibility experimentally for several hundred substances.

The dispersion methods, which start from the material of the disperse phase in bulk or in a state of division obviously coarser than the colloidal, have been divided by Svedberg into chemical and mechanical on the one hand, and electrical on the other. Instances of the former occur frequently; many cases are familiar to the analyst in which a precipitate, on being gradually washed free from the solution in which it was formed, becomes sufficiently disperse to "pass through the filter." Some metallic sulphides are conspicuous examples. In other cases precipitates can be dispersed by the action of electrolytes, a procedure already employed by Graham, and called by him "Peptization." A good example is the preparation of cadmium sulphide sol. The sulphide is precipitated by treating an ammoniacal solution of cadmium sulphate with ammonium or hydrogen sulphide, thoroughly washed and suspended in water. If hydrogen is now passed through the suspension, the flocculent precipitate gradually breaks up, the liquid becomes milky and finally perfectly clear in transmitted light, the colour being a golden yellow. Mercuric sulphide sol may be prepared in a similar manner.

A method involving both chemical and mechanical treatment is that developed by Kuzel for preparing sols of various metals, such as uranium, tungsten, vanadium, etc. The material is first ground as finely as possible, and is then digested alternately with dilute acid, water and dilute alkali. After a number of treatments it disperses spontaneously in distilled water. The tungsten obtained from such sols by coagulation was used for making "squirted" filaments for incandescent lamps before the methods of

drawing tungsten wire, which are now employed, had been developed.

In some cases an appreciable proportion of material may be reduced to colloidal sizes merely by prolonged grinding. The requisite degree of fineness is best secured by "diluting" the material to be dispersed with some other solid, which can be removed afterwards by an indifferent solvent other than the dispersion medium to be used eventually. This method has not yet been studied extensively. (*cf.* The Svedberg, "The Formation of Colloids," J. and A. Churchill, 1921).

Among the electric dispersion methods the disintegration in the electric arc is by far the most interesting. This was first studied by Bredig (1898) who found that, when a (continuous current) arc was produced under water between electrodes of the noble metals, the liquid became deeply coloured and showed all the properties of colloidal solutions as then known. Some metals only gave coarse dispersions, while others were oxidised, hydroxide sols being formed. In most cases a very slight concentration of alkali in the water is favourable or even indispensable if stable sols are to result.

The dispersion by the electric arc was further developed and investigated exhaustively by Svedberg. Instead of the continuous current he used various other types of discharge, *e.g.*, oscillating, employed electrodes of metals which do not disintegrate, such as iron or aluminium, between which the metal to be dispersed was suspended as foil or fragments, and carried out the dispersion in a number of organic liquids. He succeeded in producing sols of the alkali metals and the metals of the alkaline earths at very low temperatures. For details of these researches and their bearing on the theory of sol formation the reader is referred to Svedberg's book quoted above.

While the definition of the condensation methods is unambiguous, it is by no means certain that the dispersion methods really lead in one step to the formation of colloidal particles. This question has received a good deal of attention as far as disintegration by the arc is concerned, and there is strong evidence that the process may consist, at any rate in part, in the formation of metallic vapour and its subsequent condensation to colloidal particles. The actual mechanism of peptization is also in need of elucidation.

CHAPTER VI.

THE suspensoid sols, whatever the disperse phase, show a reasonable uniformity in their behaviour, so that it is possible to summarize their more important properties. The first to claim our interest are the fundamental properties of liquids, surface tension and viscosity. The former does not differ appreciably from that of the dispersion medium. As regards the latter, the concentration of disperse phase is, generally speaking, so low that the viscosity of a suspensoid sol is very slightly higher than that of the dispersion medium, so that quantitative investigation—if the differences are to be decidedly in excess of the experimental errors—is confined to the sols which can be obtained in exceptional concentration, or to suspensions of particles of much larger than colloidal size. Among the former must be mentioned Sven Oden's sulphur sols: two series of viscosity measurements given in his monograph on "Colloidal Sulphur," already referred to, are of special interest, as they were carried out on sols having particles of very different size, viz., about 100 $\mu\mu$ in A and about 10 $\mu\mu$ (estimated) in B. The table gives the percentage *by volume* of disperse phase and the relative viscosities, that of water at the same temperature being taken as unity. The results are plotted in Fig. 7.

Per cent. of disperse phase.	η_A	η_B
5	1·20	1·30
10	1·50	1·72
15	2·00	2·38
20	2·75	3·63

It will be seen that the sol with the smaller particles has the higher viscosity throughout, and that in both sols the viscosity increases more rapidly than the concentration of disperse phase. The latter result was also obtained by Humphrey and Hatschek in a series of measurements on a very coarse system (rice starch suspended in a mixture of carbon tetrachloride and toluene of the same density) carried out at very low rates of shear. The viscosity increased more rapidly than the percentage of disperse phase, and, in addition, was found to vary

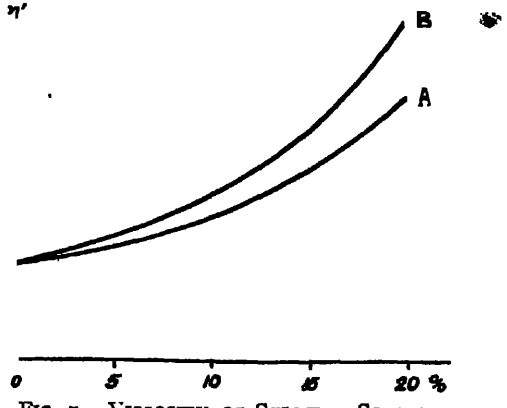


FIG. 7.—VISCOSITY OF SULPHUR SOLS OF DIFFERENT DEGREES OF DISPERSITY.

with the rate of shear, so that the complete viscosity values lie on a surface, the other co-ordinates of which are the concentration of disperse phase and the shear gradient.

The first mathematical treatment of the problem was given by Einstein (1906), who deduced the viscosity of a suspension of rigid spheres suspended in a liquid from the fundamental equations of hydrodynamics. If we call η the viscosity of the dispersion medium, η' that of the disperse phase, and

K the ratio volume of disperse phase/total volume Einstein's formula is

$$\eta' = \eta (1 + 2{\cdot}5K).$$

This means that the viscosity *increases in linear ratio with the percentage of disperse phase* and, since the radius does not appear in the equation, *that it is independent of the size of the particles.*

For low concentrations and microscopic particles the formula holds approximately, as was first shown by Bancelin (1911) on suspensions of gamboge particles. For sols and especially for higher concentrations, however, as appears from Oden's and other measurements, the increase is much more rapid than linear and is not independent of the size of the particles. A discussion of the causes of this discrepancy is beyond the scope of this work, but one difficulty in the way of applying any mathematical deduction may be pointed out. The latter must inevitably rest on ratios of volumes, whereas we know with certainty only the *weight* of disperse phase: the volume calculated therefrom on the assumption that the density of the particles is the same as that of the material in bulk need not be, and probably is not, correct. In addition, there is a strong probability that the particles may carry with them envelopes of dispersion medium, which would contribute to the effective volume.

Quite recently (1920) an attempt has been made by R. W. Hess to deduce synthetically a formula for the viscosity of a suspension of rigid particles. He arrives at the following expression:—

$$\eta' = \eta \cdot \frac{1}{1 - aK}$$

in which the symbols have the same meaning as above, and a is a "supplementary factor" always > 1, which varies with the shape, size and number of particles, and probably with the rate of shear.

The formula is not linear and, with a variable a, can be made to fit any viscosity-concentration curve very closely; whether definite relations between the variables mentioned and the value of a can be deduced, remains to be seen. Hess himself has tested the formula on suspensions of red blood corpuscles, which are not only large (7·5 μ maximum diameter) and of peculiar shape, but also easily deformable. A recent investigation by Lüers and Schneider (*Koll.-Zeitschr.* 27, 273, 1920) shows that the viscosity of a given suspension—flour—can be represented by the formula with a reasonably constant value of a.

The temperature coefficient of the viscosity of suspensoid sols or coarser suspensions is practically that of the dispersion medium, in striking contrast with most emulsoid sols.

As regards the optical properties, we are already familiar with the Tyndall cone, which is visible in practically all suspensoid sols. It may appear either merely turbid, or show a colour different from that of the sol in transmitted light, *e.g.*, the cone appears greenish in some red gold or brown silver sols. The light emitted by the Tyndall cone is plane polarized, as can easily be demonstrated by observing it with a suitable analyser, *e.g.*, a Nicol prism. The percentage of light polarized depends on the size of the particles and increases as they become smaller. The position of the plane of polarization varies with the nature of the disperse phase, more particularly with its electrical conductivity: it is perpendicular with the axis of the beam for dielectrics and oblique for metals.

The most striking optical property of sols is their colour. In many cases this is more or less the same as that of the disperse phase in coarser states of division, for instance, in the sulphide sols. There is usually no change of colour on coagulation in this

type, only an increasing turbidity; nor do sols in which the size of the particles has been varied by known methods differ appreciably in colour. It has, however, been shown by Auerbach (*Koll.-Zeitschr.*, *27*, 223, 1920), that a non-metallic sol, that of sulphur, may show a great range of colours in suitable conditions.* A dilute solution of sodium thiosulphate is decomposed by phosphoric acid, the concentrations being so adjusted that the whole process takes 15 to 25 minutes to complete itself. During that time the colour of the mixture in transmitted light changes from a pale yellow through orange, red and purple to a pure blue, the change in colour being due apparently merely to the growth of the sulphur particles. No other instance of a sol, in which the disperse phase is a dielectric, showing polychromy has so far been described.

In metal sols the colour may vary very considerably: thus, gold sols may be green (unstable), blue, violet, purple to bright ruby red. The red and purple sols turn blue on addition of electrolytes, and eventually deposit a blue sediment: the colour change is accompanied by an aggregation of the particles into larger complexes. A blue gold sol prepared directly, say by reduction with hydrazine or hydroquinone, has not necessarily larger particles than, say, the coagulum of a purple sol prepared by another method, and the question of colour in this case is complicated by the possibility of incomplete reduction; in other words, the disperse phase may not be metal, but a mixture of metal and oxide, or of several oxides. For gold this may be easily demonstrated as follows: a dilute solution of gold chloride (1/20,000) containing a little dextrin is reduced with a few drops of dilute hydroquinone solution, when a beautiful dark blue sol is formed. If this

* A similar result had been obtained earlier by Keen and Porter (*Proc. Royal Soc.*, A, Vol. *89*, 372, 1914).

is now heated to boiling and a little caustic alkali is added, the dextrin completes the reduction and the sol turns red. Of course, this red sol can be obtained directly by reduction with dextrin and alkali, and the colour is very much the same in both cases.

Silver sols may also be obtained in a great range of colour, from blue through purple, and red to pale yellow. The same possibility, incomplete reduction, has to be borne in mind in this case too.

We now proceed to consider the most striking—and most thoroughly investigated—property of suspensoid sols, their behaviour towards electrolytes, to which a special chapter must be devoted.

CHAPTER VII.

As stated in Chapter IV., the particles of a suspensoid sol are electrically charged, and this charge in some way determines the stability of the sol, since on its being neutralized by suitable means, *e.g.*, the addition of electrolytes, the sol becomes unstable, and the disperse phase is eventually precipitated. The mechanism of this stabilizing action is not by any means clear, but there is no doubt whatever of its existence. If a sol is observed in the ultramicroscope, no collisions between particles will be noticed notwithstanding their vigorous motion; on addition of an electrolyte, however, the particles will be seen to unite into larger aggregates. A very considerable amount of research has been devoted to the determination of the minimum concentrations of different electrolytes which produce coagulation in a given sol. The first thing to be noted is that coagulation has to be defined arbitrarily or conventionally, either as a colour change where this occurs, or as incipient or complete sedimentation of the disperse phase, *within a specified period of time.* Under strictly uniform conditions comparable results can be obtained, and the pioneer work of Schultze, Linder and Picton, and Hardy may be summarized as follows :—

Coagulation is chiefly determined by that ion of the electrolyte which carries a charge *opposite* to that on the disperse phase. If the latter, as in the majority of the suspensoid sols, is negatively charged, the determining ion is therefore the cation of the electrolyte.

The electrolyte concentration necessary to produce

coagulation is the lower the higher the valency of the active ion. It decreases much more rapidly than the valency increases.

A certain minimum concentration of electrolyte is necessary to produce coagulation at all.

The coagulating ion is found in the coagulum, equivalent amounts of different ions being carried down by it.

To give some idea of the general order of magnitude of the concentrations of different electrolytes, a few selected results obtained by Freundlich with an arsenious sulphide sol are here given: the electrolyte concentrations are given in millimoles per litre, and refer, of course, to the mixture sol + electrolyte:—

KCl	49·5	$MgCl_2$	0·717	$AlCl_3$	0·093
NaCl	51·0	$CaCl_2$	0·649	$Al(NO_3)_3$	0·095
LiCl	58·5	$Ba(NO_3)_2$	0·687		

It will be noticed that (1) ions of the same valency coagulate in approximately the same concentration, and (2) the concentration of univalent ion required to produce coagulation is roughly 70 times that of bivalent, and 560 times that of trivalent ion. If we call the coagulating concentrations of the three ions respectively C_1, C_2 and C_3, where the index represents the valency, we can therefore write approximately:—

$$C_1 . C_2 : C_3 = 8 \cdot 3^3 : 8 \cdot 3^2 : 8 \cdot 3$$

$(8 \cdot 3^3 = 590,\ 8 \cdot 3^2 = 71)$.

An empirical relation of this kind—the numerical constant, of course, differs considerably from one sol to another—had been found by Schultze and by Hardy:—

$$C_1 : C_2 : C_4 = k^3 : k^2 : k$$

Whetham investigated the problem mathematically in 1899 and deduced a formula similar to the above from kinetic considerations.

This comparative simplicity is, however, found to prevail only when suitably chosen values are compared. Considerable divergences manifest themselves when the field of investigation is extended. Ions *of the same valency and combined with the same anion* differ very considerably in their coagulating power. It was found at an early date that hydrogen ion—to confine the comparison to cations for the moment—was effective in lower concentrations than other cations combined with the same anion, *i.e.*, that acids coagulated in lower concentrations than their salts with univalent cations. A few comparative values determined by different observers are given to illustrate this point:—

Mastic sol (Hardy).		Gold sol (Hardy).		As_2S_3 sol (Freundlich).	
HCl	0·004	HCl	0·008	HCl	0·031
NaCl	0·12	NaCl	0·013	NaCl	0·051
$BaCl_2$	0·022				

Hardy's data are given in gm. equivalents per litre, and Freundlich's figures have been reduced to the same unit. In all three cases HCl coagulates in considerably lower concentration than does NaCl; moreover, the mastic sol is coagulated by H ion in *lower concentration than by the bivalent* Ba ion. The latter anomaly is by no means isolated.

Organic cations, which were first investigated extensively by Freundlich, also coagulate in much lower concentrations than inorganic ions of the same valency. Three of Freundlich's values for the alkali chlorides are repeated below, and the coagulation concentrations for three chlorides with organic univalent cations are given for comparison:—

As_2S_3 sol as above.

NaCl ..	51·0	Aniline chloride	2·52
KCl ..	49·5	Para-chloraniline chloride	1·08
LiCl ..	58·5	Morphine chloride ..	0·425

It will again be noticed that the last-named chloride coagulates in a concentration appreciably lower than even that of the chlorides with bivalent cations.

If we confine ourselves to the consideration of any one cation, we find that the concentration required to coagulate a given sol varies very markedly according to the nature of the anion with which it is combined. The following figures found by Freundlich with the arsenious sulphide sol already referred to show the effect of the anion very strikingly :—

1/3K Citrate	240
$KC_2H_3O_2$	110
$KCHO_2$	86
$1/2K_2SO_4$	65·5
KNO_3	50·0
KCl	49·5

It is obvious that the anion exerts some effect on the phenomenon, which is apparently antagonistic to that of the cation, and does not depend very clearly on valency. Whatever it is, it cannot be separated from that of the cation, and this is probably one of the reasons why attempts to deduce a general valency rule, in which the active ion alone is taken into account, must fail. A further reason for this failure is the existence of obvious specific differences between various types of cations. These make comparison between ions of the same valency impossible unless they are closely related. For ions permitting such a comparison and combined with the same ion, the valency rule is a useful guide, though for any given sol it will still require verification in detail.

Two points of interest have not been touched on so far : the effect of the concentration and of the degree of dispersity of the sol on the electrolyte concentration necessary to produce coagulation. As regards

the former, information is scanty, being derived principally from some experiments by Freundlich, who finds that the electrolyte concentration increases with, and is roughly proportional to, the concentration of disperse phase. The second point has been elucidated chiefly by Sven Oden, who devised methods of obtaining sulphur sols with particles of uniform size, which could be varied within wide limits. (In sols prepared in the usual way, and without subsequent treatment, the particles are generally of different sizes.) Oden found that for equal concentration by weight of disperse phase, the electrolyte concentration necessary for coagulation *increased with decreasing size of the particles*—in other words, the higher the degree of dispersity the greater the stability of the sol.

We have so far referred only to negatively charged particles and to cations. It follows by analogy that, with positively charged particles, the active ion should be the anion, and that, therefore, the valency of the latter should be the factor determining the electrolyte concentration. The principal sols in which the disperse phase is positively charged are—apart from a few dyes like Night Blue—the hydroxide sols, which we shall treat separately for certain reasons. Some of them, however, show distinct suspensoid character, and behave towards electrolytes in the manner just anticipated, as will be seen from the following concentrations required to coagulate ferric hydroxide sol, also determined by Freundlich: the concentrations are given in millimoles per litre:—

KCl	9·03	K_2SO_4 ..	0·204
KNO_3 ..	11·9	$MgSO_4$..	0·217
$1/2BaCl_2$..	9·64	$K_2Cr_2O_7$..	0·194
$1/2Ba(OH)_2$..	0·42		

It will be noticed that the concentration depends

principally on the anion, that the bivalent anions coagulate in much lower concentration than the univalent ones, and that among the latter the OH ion again occupies an exceptional position, as does the H ion among the cations.

Electrolyte coagulation—which as far as the results quoted hitherto go may be loosely defined as agglomeration of the particles into aggregates of sufficient size to show sedimentation within a limited time—is a process requiring time, and recent research has been devoted to studying the *velocity* of the process. We can only describe very briefly the first of these investigations, carried out by Paine (1912) with a copper oxide sol obtained by Bredig's method and carrying a positive charge. Very rapid coagulation and settling could be produced, after the addition of electrolyte, by heating the mixture for a short time. The procedure adopted accordingly consisted in adding to a given volume of sol known amounts of electrolyte, removing samples at known intervals, heating these to produce sedimentation and determining the amount of copper still remaining in the clear supernatant liquid. The principal results are as follows: (1) there is a latent period after the addition of electrolyte during which no coagulation occurs; (2) coagulation, once begun, proceeds first rapidly and then with decreasing velocity; (3) the velocity increases with the electrolyte concentration; and (4) for two different electrolyte concentrations, the times required to reach the same stages in coagulation are in constant ratio, *i.e.*, if the electrolyte concentration A takes twice as long as B to coagulate, say, 25 per cent. of dispersed phase, A will also take twice as long as B to coagulate 50 or 75 per cent., etc. The results are shown graphically in Fig. 8, in which the amount of copper still remaining in the sol is plotted as ordinate against the time as abscissa. Two curves are given, for two electrolyte concentra-

tions, and the statement under (4) can be expressed thus: the abscissæ of pairs of points on the two curves which have the same ordinate are in constant ratio:

$$AB/AC = A'B'/A'C' = A''B''/A''C''.$$

These results have been generally confirmed by subsequent investigations, among which those by Freundlich and by Zsigmondy, with various colla-

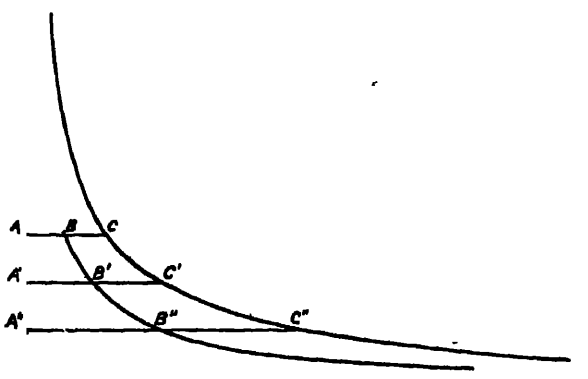


FIG. 8.—CURVES ILLUSTRATING RELATION BETWEEN COAGULATION VELOCITY AND ELECTROLYTE CONCENTRATION.

borators, must be mentioned. The problem of coagulation velocity has also been treated mathematically by v. Smoluchowski, his theoretical conclusions being in good agreement with Zsigmondy's experimental results. It is worth mentioning that the mathematical treatment involves no assumptions, and throws no light, on the actual process of the removal of the electric charge, but starts from electrically neutral particles.

A brief statement of the theories which have up to the present been propounded to account for the

origin of the electric charge, as well as for the mechanism of its neutralization, will follow more conveniently when the electrical properties of emulsoid sols and the phenomenon of absorption have been discussed.

CHAPTER VIII.

ONLY one means of removing the electric charge on suspensoid particles, viz., the addition of electrolytes to the sol, has been discussed so far. Since sols with both negative and positive charges on the disperse phase are known, the idea will readily suggest itself that neutralization of the charges, followed by coagulation, may be brought about by mixing sols with opposite charges. Such a mutual coagulation (of certain dyes) was first observed by Linder and Picton (1897), who ascertained that the sols which precipitated each other carried charges of opposite signs. Similar observations were made by Lottermoser (1901) with various inorganic sols. Biltz investigated the phenomenon quantitatively and found that, when the ratio of the volumes mixed was kept within certain—fairly narrow—limits, complete coagulation of both sols took place ; if either sol was in excess of this optimum ratio, precipitation was incomplete or did not take place at all. If these uncoagulated mixtures are submitted to cataphoresis, they are found to carry the same charge as the sol which was added in excess. If two coloured sols, *e.g.*, gold and ferric hydroxide, coagulate each other completely, the supernatant liquid is perfectly colourless.

An electric charge of course exists on the contact surface of any substance with a liquid, though it does not exert perceptible effects unless this surface is large. It attains a sufficient magnitude in porous materials, such as filter paper, which becomes negatively charged in contact with water. If a strip of filter paper is partly immersed in a positive sol,

the disperse phase is therefore coagulated in the pores, and pure dispersion medium rises in the strip by capillarity. For the same reason positive sols cannot be filtered satisfactorily through filter paper.

Mixtures of suspensoid sols with sols of marked *emulsoid* character present features of great theoretical interest and of some technical importance. We have already mentioned that the latter are much less affected by electrolytes in low concentrations than are the suspensoids, and the mixture acquires this characteristic; the suspensoid sol also becomes less sensitive or, as the effect is usually described, it is "protected" by the emulsoid. The phenomenon had already been observed by Faraday, who noticed that the addition of "a little jelly" (presumably gelatin) rendered his gold sols much more stable. It can be very easily demonstrated by adding to a gold sol a small quantity of, say, gelatin or gum-arabic sol, and then an amount of electrolyte known to produce an immediate colour change in the original sol, when the protected sol will be found to be unaltered. The phenomenon has been studied quantitatively chiefly by Zsigmondy, who defines as the "*gold number*" of an emulsoid the number of milligrammes which, when added to 10 c.c. of a standard gold sol, is just insufficient to prevent a colour change on the addition of 1 c.c. of 10 per cent. sodium chloride solution. The reciprocal of the gold number is therefore a measure of the "protective effect." A number of values determined by Zsigmondy in this way are given below:—

Protective colloid	Gold number.	Reciprocal of gold number.
Gelatin	0·005 — 0·01	200 — 100
Casein	0·01	100
Gum-arabic ..	0·15 — 0·5	6·7 — 2·0
Gum-tragacanth ..	2·0	0·5
Dextrin	6 — 20 .	0·17 — 0·05

As the gold numbers represent milligrammes in 11 c.c., or grammes in 11 litres, it is evident that the concentrations of even inferior protecting agents like the gums are very low, while those of gelatin are exiguous. It must be added, however, that the protective effect is markedly specific with reference to the sol; if another sol is substituted for gold sol, the concentration of any given colloid, and even the order in which the gold numbers increase, may vary considerably.

The protective effect may also manifest itself in another way by preventing the formation of a precipitate with particles exceeding colloidal size as the result of a reaction which, in the absence of the protective agent, produces a coarse precipitate. Sols of a great variety of substances may be obtained in this way, by carrying out the necessary reactions in the presence of gelatin or gum-arabic, and the concentration of disperse phase can be increased much beyond that obtainable without protection. In many cases the sols thus made possess a further characteristic of the protective agent, viz., they may be dried and the residue redisperses in water or other dispersion medium. One group of compounds, which shows this effect to a marked degree, has acquired great prominence in recent years. These are certain products of the hydrolysis of albumin by alkali, first described by Paal and his collaborators as " protalbic " and " lysalbic " acids, and used by them in the preparation of a very large number of metal and other sols.

Amberger (1912) has shown that wool fat may act as a protective agent in organic liquids, in which it is soluble, and has prepared various " organosols " of the noble metals by its aid. The preparation of silver sol is a good instance of the method. A concentrated solution of silver nitrate is thoroughly incorporated with wool fat (which, as is well known,

absorbs a large volume of water) and then an equivalent amount of caustic soda solution. The silver oxide formed is, under the influence of light, reduced by some of the constituents of the fat; the whole mass is then dissolved in chloroform and shaken out with calcium chloride to remove water and reaction products. The chloroform sol on evaporation leaves a salve-like residue, which disperses in any solvent for wool fat to form a dark brown and extremely stable silver sol.

The mechanism of protective action is by no means clear. The theory suggested by Bechhold, that the suspensoid particles are coated by the protective colloid, is difficult to reconcile with the ratios of the numbers and volumes of particles in highly disperse systems, though it may quite possibly hold for coarser systems. That particles of one colloid aggregate with a number of particles of the other is maintained by Zsigmondy, as the outcome of ultra-microscopic observation, but this does not explain how the action of electrolytes on the complexes is prevented. The matter is still further complicated by some observations made by Wo. Ostwald (*Koll. Beih.* 10, 179, 1919) on Congo-Rubin, the red sodium salt of a blue acid. Solutions of the dye show typically suspensoid character and undergo a colour change very similar to that of red gold sols on the addition, not only of acids which may be held to liberate the dye acid, but of neutral salts and even of barium hydroxide. Ostwald finds that Congo-Rubin sols can be protected *after the addition of the electrolyte—i.e.*, when the protective colloid is added to a sol which has been turned purple or blue by electrolyte, the colour returns to red. It is difficult to reconcile this result—which by the way does not appear to have been duplicated in the case of any other sol—with any existing theory of protective action.

CHAPTER IX.

We now proceed to the description of a few typica hydroxide sols, a class exhibiting such a variety of behaviour, especially towards electrolytes, as to justify their separate treatment. In all cases in which a coagulum is produced by electrolytes this does not, as in the case of typical suspensoids, consist of the material of the disperse phase only but is heavily hydrated; in a number of cases no macroscopic separation of disperse phase occurs, but the whole system sets to a gel, indicating emulsoid character. The methods used in preparing them are, as in the case of suspensoids, either condensation or dispersion methods, and among the latter peptization by suitable agents plays a considerable part.

Sols of aluminium, ferric and chromic hydroxide were prepared by Graham by the same method; the freshly precipitated hydroxide was dissolved in a solution of the chloride and dialysed. An alternative procedure in the case of ferric hydroxide consists in adding a solution of ammonia or ammonium carbonate to ferric chloride solution as long as the precipitate redissolves, and then dialyzing. The sols are perfectly clear liquids and are very sensitive to electrolytes, more particularly the $Al(OH)_3$ sol.

The latter can also be made much more expeditiously by another peptization method due to A. Muller. Aluminium hydroxide is precipitated from hot dilute aluminium chloride or sulphate solution by ammonia, washed rapidly, and then suspended in water. Dilute hydrochloric acid (N/20)

is now added in lots of 1 or 2 c.c. at a time, and the mixture heated to boiling after every addition, evaporated water being replaced. The precipitate gradually disperses, and an opalescent sol results. Thorium hydroxide sol may be prepared by an exactly analogous manner.

The three sols mentioned are positively charged and it is therefore the nature, and more particularly the valency, of the anion which determines the concentration required to produce coagulation.

A negatively charged hydroxide sol with interesting properties is that of stannic acid, which had also been prepared and studied by Graham; more recently it has received a good deal of attention from Zsigmondy and his school. The simplest way of obtaining it is as follows: a solution of sodium stannate is decomposed by a solution of sodium hydrogen carbonate, the precipitate well washed, suspended in water, and peptized with 2 or 3 c.c. of ammonia solution. The precipitate gradually disperses, the liquid becoming first opalescent and finally colourless and clear as water. Very small amounts of almost any electrolyte produce a copious flocculent precipitate. Notwithstanding this high sensitiveness the sol shows one of the properties of emulsoid sols: it exerts a marked protective action on suspensoid sols. If a mixture of stannic acid sol and red gold sol is coagulated by an electrolyte, a *red* precipitate results: in other words, the stannic acid has prevented the coagulation of the gold while carrying it down with it. It has been shown by Zsigmondy that this precipitate is identical with the purple of Cassius, *i.e.*, the precipitate obtained by reducing gold chloride with stannous chloride. The latter, as well as the coagulum from stannic acid and gold sol, may be peptized by ammonia. Analogous precipitates may be obtained from mixtures of stannic acid sol with silver, platinum and, as Ostwald has shown, Congo-Rubin sol.

A number of hydroxide sols of the tri- and quadrivalent metals may be prepared through the hydrolysis of their nitrates, acetates or chlorides, a procedure which falls under the head of condensation methods. Aluminium hydroxide sol may be obtained, as a slightly opalescent liquid, by prolonged boiling of a dilute solution of aluminium acetate. Another instance is Krecke's method of preparing ferric hydroxide sol: if a few c.c. of 30 per cent. solution of ferric chloride are added to about 500 c.c. of boiling water, the mixture turns reddish brown and perfectly clear in transmitted as well as reflected light. The HCl formed by the hydrolysis may be removed by dialysing while still hot.

In the case of some nitrates hydrolysis is sufficient at ordinary temperature, and it is only necessary to dialyse their solutions against water to obtain the hydroxide sols. Probably the most interesting of these is the sol of ceric hydroxide, first prepared by A. Muller by dialysing an 11 per cent. solution of ceric ammonium nitrate against water for four days. The sol is a clear, yellow liquid, which on addition of electrolytes sets to a clear gel. The sensitiveness to the latter is remarkable; a concentration of about 20 millimoles of sodium chloride is sufficient to produce gel formation within a few minutes in a sol dialysed to a sufficient extent. An interesting property of the sol is that, either by ageing for several months, or by heating to 100° C. for only 30 minutes, it loses the power of forming a gel, but gives a precipitate on the addition of electrolytes. This is no doubt due to gradual dehydration of the disperse phase, a change which can be traced by viscosity measurements. The sol has been studied in great detail by Pauli and Fernau (*Koll.-Zeitschr.*, *20*, 20, 1917).

As is evident from this short survey, the metallic hydroxide sols exhibit a considerable variety of

behaviour. Those described are positively charged with the exception of stannic acid, and are, generally speaking, very sensitive to electrolytes. As far as the effect of valency has been studied—chiefly for ferric hydroxide, and to a smaller extent for aluminium hydroxide—it agrees with that found to hold for negative suspensoid sols; the anion is the ion which determines coagulation (or gel formation), and bivalent anions act in markedly lower concentration than univalent ones. Ions of higher valency, like $Fe(CN)_6''''$, precipitate in extraordinarily low concentrations and have not been studied quantitatively. While the electrical properties are thus fairly uniform, is is obvious that a further factor, viz., hydration of the disperse phase, plays an important part, as it does in the systems of undoubted emulsoid character.

CHAPTER X.

We have so far considered typical suspensoids, in which the disperse phase consists of solid, or more correctly rigid, particles, and a few metallic hydroxide sols, in which the disperse phase is undoubtedly heavily hydrated, so that they form a gradual transition to the emulsoid systems. To gain a deeper insight into the properties, more especially the physical ones, of systems of two liquid phases, it is necessary to consider dispersions, both phases of which are known to be liquid in bulk and under ordinary conditions of temperature, etc. Such dispersions of one liquid in another, in which it is practically insoluble, are known as "emulsions," and play an important part in nature and in the arts. The best known natural emulsion is milk, which contains fat globules dispersed in a solution of caseinogen, albumin, sugar and various salts. As regards artificial emulsions, some of them are unwelcome by-products of various industrial processes, such as the condense water from reciprocating steam engines, which contains a portion of the oil used for cylinder lubrication in a state of very fine and persistent division, or wool washings, in which some of the wool fat is emulsified by the action of soaps formed from certain constituents of the fat. A large number of emulsions are also prepared purposely; mayonnaise sauce, an emulsion of oil in yolk of egg, is a familiar and very instructive example, while others are well-known pharmaceutical preparations, certain "solid" lubricating compounds, etc.

The simplest systems of this class are the pure

"oil-water" emulsions, in which, as the name implies, the continuous phase is water not containing any solute. The type of these is engine condense water, with about one part of oil in 10,000 of water; very similar emulsions may be obtained by pouring a dilute solution of an oil in alcohol or acetone into a large volume of water, when the oil separates in the form of minute globules, generally less than 1 μ diameter. In this way it is possible to obtain stable emulsions containing up to 1/1,000 part of oil.

This great dilution is quite in keeping with what we already know about suspensoids, and investigation of such emulsions, which has been carried out during the last ten or twelve years by Donnan, Lewis, Ellis and Goodwin, and the author, shows that they do not differ very materially from systems with solid particles. The oil globules show active Brownian movement, and are coagulated by electrolytes, acid being effective in very much lower concentrations than salts of univalent, and even some bivalent cations, the charge on the oil globules being negative. They further resemble solid particles, inasmuch as they can be retained by ultra-filtration, as was first shown by the author. This means that the globules, although liquid, require a considerable pressure to be deformed sufficiently to enter the capillaries of the septum. Mathematical investigation by the author, which is in very good agreement with experimental results, has shown that this "*quasi*-rigidity" of the particles is due, and simply proportional, to their interfacial tension against the dispersion medium, which resists deformation and the consequent increase of surface. Oil globules having a diameter of about 0·8 μ and an interfacial tension (against water) of about 40 dynes/cm. require a pressure of over 5 atmospheres to force them into pores of half that diameter filled with water. For mercury globules of the same size, but with an inter-

facial tension of about 370 dynes/cm. the pressure would be nine times that for oil globules, so that the mercury globules would be, from this aspect, indistinguishable from solid spheres. If the liquid state of the disperse phase is to show itself, a further condition must be satisfied, viz., the interfacial tension of the two phases must be low.

This will become still clearer from the following considerations. The phase ratio in the case of solid particles is obviously limited by their shape. If we take the simplest case, spherical particles of equal diameter, the closest packing possible is reached when each sphere touches 12 others, in which case the spheres occupy about 74 per cent. of the total volume and the ratio: volume of disperse phase/volume of continuous phase is therefore about 74/26. Such an arrangement of *solid* particles, however, no longer has the properties of a liquid, but will be a mud or paste which may retain its shape. If the disperse phase, however, is liquid and easily deformed, there is obviously no upper limit to the phase ratio; when the ratio 76/24 is reached the globules will just touch, and when it is exceeded they will become flattened at the 12 points of contact, and develop the faces of the rhombo-dodecahedron. As this development of polyhedral shape involves an increase of surface, it is opposed by the interfacial tension of the phases and becomes possible only if this is low. In that event there is physically as well as geometrically no upper limit to the phase ratio; as a matter of fact emulsions containing 99 per cent. of disperse oil in 1 per cent. of soap solution have been prepared by Pickering.

It is, generally speaking, quite impossible to make emulsions containing such high percentages of disperse phase (or, indeed, anything more than fractions of 1 per cent.) in an aqueous dispersion medium, unless the latter is a solution of certain substances,

such as a soap, various products of the saponification of albumin or other proteins, or one of the saponins. All these solutions have one characteristic in common: they froth strongly even in great dilution. Frothing, which never occurs in pure liquids, is a definite indication that the dissolved substance lowers the surface tension of the solvent, and this lowering, which generally is parallel with a lower interfacial tension against a second liquid, is intimately connected, not only with the possibility of highly-concentrated emulsions discussed above, but with the process of emulsification. This connection can be easily demonstrated with the drop pipette as modified by Donnan, illustrated in Fig. 9. A pipette A is provided with a length of capillary tube B, the object of the latter being to restrict the flow. The bend C ends in a point D, which is ground off flat. The pipette is filled with the oil to be examined and the outlet submerged in the solution which is to form the continuous phase. The size of the drop which issues from D is determined on the one hand by the difference in density of the two liquids, which tends to tear it off, and on the other by the interfacial tension acting round the circumference of the orifice, which tends to retain it. Any decrease in interfacial tension accordingly shows itself in reduced size, or increased number, of drops, and the parallelism between it and the emulsifying power of the solution is very marked. To give a numerical instance, a pipette used by the author gave 65 drops of light petroleum in water, and 260 drops of the same oil in 1 per cent. soap solution. With such a soap solution it is quite easy to make emulsions containing 80 per cent. of petroleum as disperse phase.

We can now form a picture of the various factors which make possible the existence of these high percentage emulsions and give them their highly

characteristic properties. The oil globules are no longer spherical but polyhedral, the adjoining faces

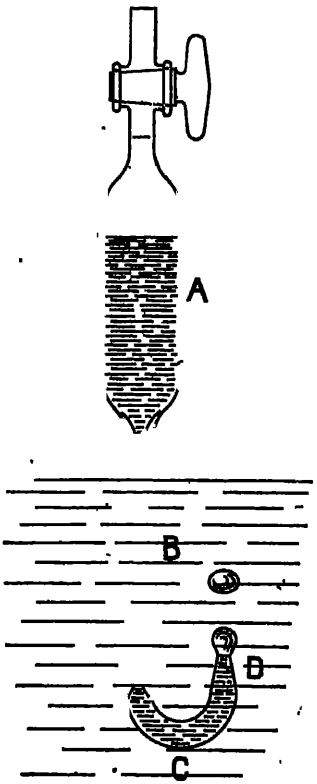


FIG. 9.—DONNAN'S DROP PIPETTE.

being separated by very thin films of the disperse phase. Such films would tear if they had the high surface tension of water, and can persist only if the interfacial tension is very greatly lowered by the

dissolved substances mentioned above. If the films are thick, *i.e.*, if the particles are widely separated, a persistent emulsion is possible even in pure water. At the same time, the low interfacial tension alone does not appear sufficient to prevent the eventual fusion of contiguous globules of disperse phase, and several investigators, especially W. D. Bancroft, have arrived at the conclusion that the particles must be surrounded by a film having certain definite properties, into which we cannot enter. Such a film may be the result of adsorption from a solution (see Chapter XXI.), or it may even consist of a finely divided solid. Pickering showed that if certain basic sulphates of heavy metals are shaken up with water and oil, the latter is dispersed in the former as a stable emulsion. Conversely Schlaepfer (*Jl. Chem. Soc.*, *113*, 522, 1918), was able to produce an emulsion of *water in oil* by shaking the two liquids with lamp black. The type of emulsion formed evidently depends on whether the finely-divided solid is more easily wetted by one phase than by the other, and the liquid which wets less becomes the *disperse* phase, viz., oil with the basic sulphates, and water with lamp black. The theory of the phenomenon is treated at greater length in the companion volume on "Surface Tension and Surface Energy," by R. S. Willows and the author.

If the emulsifying agent is destroyed, for example, by adding a mineral acid to an emulsion of oil in soap solution, the disperse phase coalesces immediately and eventually separates completely. This segregation is of course simply the result of the great increase in interfacial tension when, say, sodium chloride is formed from the sodium oleate present on the addition of hydrochloric acid. A phenomenon of great interest, and less easy to explain, was first observed by G. A. Clowes. An emulsion of a glyceride, *e.g.*, olive oil, can easily be

made by shaking it with very dilute caustic soda, the small amount of oleate formed acting as emulsifying agent; the oil becomes the disperse phase. If an equivalent amount of calcium chloride is added to the emulsion, the phases are *reversed*, the oil becoming the continuous, and the aqueous solution the disperse phase. Other electrolytes have been systematically studied by Bhatnagar (*Gen. Disc., Faraday Soc.*, October, 1920), but the theory of this interesting phenomenon cannot yet be said to be clear.

Generally speaking, we find that emulsions group themselves, as far as the conditions for stability are concerned, into two classes. In the pure oil-water emulsions, as in the suspensoids, the stabilizing factor is undoubtedly the electric charge. In the concentrated emulsions made with an emulsifying agent the electric conditions have hardly been investigated and can only play a secondary part: the stability depends on other physical properties of the continuous phase, and probably on the nature of some film formed at the boundary of the two phases.

The viscosity of emulsions has received very little quantitative study, but it is known to increase very rapidly with the percentage of disperse phase. A marked difference between a suspension of rigid particles, and an emulsion can, in the nature of things, be expected to show itself only when the globules of disperse phase approach contact, *i.e.*, when the disperse phase amounts to more than 70 per cent. of the total volume.

The question now arises how far the considerations on the properties of systems of two—known—liquid phases may be transferred to, or help to elucidate, the properties of emulsoid sols, in which the liquid state of the dispersed phase is merely an inference. It is fairly obvious that another factor

must be presumed, more especially from considerations of viscosity. We have already seen that small concentrations of emulsoid colloids, such as gelatin, rubber or nitro-cellulose, may produce sols of very high viscosity; on the other hand, we see in the case of emulsions, that a high viscosity is caused only by a large *volume percentage* of disperse phase. We are therefore forced to the conclusion that a small amount of dry emulsoid may produce a large volume of disperse phase in the sol, by hydration or solvation, that is by associating with itself a large portion of the solvent. The evidence for this condition is varied and conclusive, and we shall further see that the state of hydration is also intimately connected with the electric condition of the disperse phase in a number of sols. Individual sols show—compared with the striking uniformity of suspensoid sols—a bewildering variety of behaviour, and must therefore be studied separately. As a first representative of the class we will consider the principal inorganic emulsoid sol, that of silicic acid.

CHAPTER XI.

"SOLUBLE" silicic acid was known already to Berzelius, who obtained it by treating silicon sulphide with water. Hydrogen sulphide is liberated and the silicic acid formed at the same time remains in solution. Berzelius also noticed that more concentrated solutions became gelatinous after a time. These observations were repeated by Frémy, who found that the addition of alkali salts caused the solution to gelatinize.

The silicic acid sol was studied extensively by Graham. He prepared it by pouring a solution of sodium silicate into an excess of dilute hydrochloric acid, and dialyzing the mixture to remove the sodium chloride formed and the excess of acid. During the first stage of dialysis silicic acid passes freely into the outside water: the portion which thus escapes may amount to 10 per cent. of the total. The liquid finally left in the dialyzer is perfectly clear and colourless, and has a viscosity not much in excess of that of water. On keeping, or on addition of certain electrolytes, the sol becomes opalescent, the viscosity increases rapidly and the sol is finally transformed into a translucent gel. The transformation is irreversible, *i.e.*, the gel cannot be transformed back into sol by treatment with water alone.

The electrical properties of the sol and the effect of electrolytes are rather obscure, notwithstanding a considerable number of investigations devoted to them. Graham already observed that certain electrolytes produced very rapid gel formation:

ammonia, phosphates and carbonates, and even CO_2 passed through the sol, act in this fashion. Generally speaking, a small amount of acid increases the stability; this is of particular interest, since Billiter has shown by cataphoresis that the sol is electrically neutral with this concentration of H ion, while it is positively charged with higher $H^{\cdot}$ concentration, and negative when containing OH'. The sol accordingly appears to have a maximum of stability *at the iso-electric point*, a state of things which we shall encounter in several emulsoid sols, but one which is in sharp contrast to the behaviour of suspensoids. The effect of neutral salts has been studied by Pappada among others; here again there is a marked difference between silicic acid sol and suspensoid sols, inasmuch as very much higher concentrations are necessary to accelerate gel formation than those which produce coagulation in suspensoids. This also is a phenomenon which occurs with a number of emulsoid sols. Furthermore, a marked specific effect, especially of the anion, shows itself, which is not connected with its valency. This effect, which is of very great importance, we shall discuss in detail when describing the albumin sol, in connection with which it was first observed and has been most thoroughly studied.

The ceric hydroxide already mentioned (p. 68), while showing distinctly the character of a positively charged sol, has marked emulsoid properties when fresh. Like the silicic acid sol it sets to a gel on addition of electrolytes, but this transformation is not necessarily irreversible; a fresh gel may be peptized again by contact with the sol, or by the addition of an extremely small amount of nitric acid. We have already seen that the sol may lose the emulsoid character and eventually give a precipitate on addition of electrolytes; we shall again find parallels to this change in organic emulsoids.

An emulsoid sol showing marked indifference t electrolytes is that of tungstic acid, obtained accorc ing to Graham by adding a slight excess of dilut hydrochloric acid to a solution of sodium tungstat and dialysing the mixture. A little hydrochloric aci must be added at intervals during dialysis; a perfectly clear sol of tungstic acid finally remains which neither precipitates nor sets to a jelly on th addition of acids or neutral salts. It can be evapo rated to dryness, the residue forming transparen scales which resemble gelatin and, like the latter adhere so strongly to the glaze of the basin as to tea fragments out of it during the progress of drying. The dry acid forms a gummy mass and finally a sol with water. The resemblance to organic emulsoids like gum-arabic is thus very striking.

The three inorganic emulsoid sols described show the variety of behaviour which we shall find again, to an even more striking degree, among the important organic representatives of the class. Ceric hydroxide is distinctly a positive sol; silicic acid is also affected by electrolytes, but neither the sign of the charge nor the effects of valency are as unambiguous as with the suspensoids, while tungstic acid is apparently indifferent to electrolytes. It must be added that the last-named sol has not received attention since Graham's time.

Silicic acid sols and gels are supposed to have existed in considerable quantities at some geological periods, and various minerals, like agate and opal, probably owe their origin to such gels; some varieties of the latter contain fairly large amounts of water. Even moist deposits of silicic acid gel have been found in quite recent times in the course of tunnelling and mining operations.

CHAPTER XII.

THE organic emulsoids are very numerous and extremely important, including, as they do, most of the proteins, such as albumin, casein, glutin (gelatin), hæmoglobin, etc., a number of carbohydrates, as starch, agar, the gums, cellulose and its various esters, the soaps, etc. It is impossible within the limits of a short work to do more than select a few typical examples and to develop a number of general points of view to which their extremely varied behaviour becomes referable.

Two of these may usefully be considered together, viz., gelatin and agar, as illustrating that a marked similarity in colloidal characteristics may go together with a profound difference in chemical constitution. The former is a mixture of proteins, the principal one of which is glutin, while agar is a mixture of carbohydrates, the most important one being *d*-galactan. The two substances occur in commerce as air-dry gels; when immersed in cold water they imbibe large volumes and swell until an equilibrium is attained. On heating, the swollen gels disperse to form sols, the temperature necessary to effect this being 25° to 35° C. for gelatin, and about boiling point for agar. On cooling the sols set to translucent gels, the setting point for gelatin being a few degrees lower than the "melting point," while agar sol can be cooled to about 35° before setting. The process is completely reversible, but the gels have to be heated to the original dispersion temperatures to be transformed into sols again. The agar sol-gel transformation is thus a particularly striking example of the

phenomenon of hysteresis—which we shall encounter constantly in connection with various properties of emulsoid sols—as the sol, once formed, does not gelatinize until cooled to about 35° C., whereas the gel is not retransformed into sol unless raised to a temperature nearly 70° higher. A similar, though much slighter, hysteresis is observed with gelatin, the range being from 5° to 7°. As in the case of silicic acid the transformation of sol into gel is quite continuous *as far as it can be observed.* With falling temperature the viscosity rises quite continuously, but eventually reaches a point where it can no longer be measured by the usual methods, and a discontinuity is quite possible at or beyond this point.

Agar sol and gel have not received much study, and we shall therefore have to confine ourselves to a discussion of the properties of gelatin. A certain minimum concentration is necessary if a gel is to form at a given temperature; this varies considerably with the brand of material, but it may roughly be stated that with less than about 0·25 per cent. a gelatin sol will not set even at 0° C. At room temperature—15° C.—a concentration of something like 1 per cent. is necessary; with increasing gelatin content the "melting" and "setting" points both rise. The following data, determined by Pauli, give an idea of this connection and of the hysteresis range:—

Gelatin concentration in per cent.	5	10	15
Setting temperature ..	17·8°	21°	29·5°
Melting temperature ..	26·1°	29·6°	29·4°

The two temperatures are not sharply defined, and must be determined by strict adherence to some conventional method.

A fact of great importance is that *all the properties of a gelatin sol* depend not only on concentration and

temperature, as do those of a true solution, but to a marked degree on the previous treatment and history of the sol. The property most conveniently and accurately measured is the viscosity, although in the present state of our theoretical knowledge it is unfortunately not possible to say what physical change in the sol corresponds to a change in the viscosity coefficient. We shall return to this subject when a number of emulsoid sols have been described, but in the meantime it may be said, for instance, that the viscosity of a gelatin sol depends not only on the concentration and temperature, but also on the *age of the sol*. If a gelatin sol of such low concentration that it does not set at ordinary temperature is kept with aseptic or antiseptic precautions, the viscosity rises steadily during the first few days. In an example measured by the author the viscosity of a 0·5 per cent. gelatin sol was 969 (in arbitrary units) when the sol was 24 hours old, and 2,657 when it was 48 hours old, *i.e.*, over 2·5 as high. The viscosity of a sol even varies—all other factors being equal—according to the time which the dry gelatin has been allowed to swell in water before dispersion, and generally with every alteration in the method of preparation.

The action of electrolytes on gelatin sols is excessively complicated, and two effects have to be sharply distinguished: coagulation or precipitation, and alterations in the setting point. As regards the former, very high concentrations are required to produce a coagulum or even incipient turbidity: several moles per litre of KCl and about 0·38 moles of Na_2SO_4. The sulphates precipitate in the lowest concentration, and a sufficient addition of sodium or ammonium sulphate to a gelatin sol produces a tough and stringy coagulum, which, as mentioned above (p. 30), on standing at 30° gradually forms a liquid layer. This form of coagulation is evidently

different from that familiar to us with suspensoid sols, and depends on a withdrawal of water from the disperse phase. It is in accordance with this view that gelatin can be precipitated reversibly from its sol by non-electrolytes which withdraw water, *e.g.*, alcohol. This type of precipitation is therefore necessarily connected with the degree of hydration which in its turn depends on the electric charge of the disperse phase and becomes a minimum at the iso-electric point. Gelatin is iso-electric at a definite H concentration, which varies with different brands; Pauli ("Colloid Chemistry of the Proteins," p. 38) gives it as $1{\cdot}8 \times 10^{-5}$ for a 1 per cent. sol of the gelatin examined by him. At this point the sol is most easily precipitated by alcohol and the viscosity—which undoubtedly increases with hydration of the disperse phase, though the function connecting the two is not known—shows a decided minimum.

The effect of neutral salts on the setting temperature and setting velocity has been studied by several observers. A marked influence of the anion is unmistakable: sulphates and acetates raise the setting point, compared with that of the aqueous sol, while nitrates, iodides and thiocyanates lower it. Incidentally it may be mentioned that these anions have a very similar effect on agar sols, and, as far as a parallel is possible, on silicic acid sol, so that the effect is certainly not chemical or in any way specific to gelatin. Ten per cent. sols of gelatin about half-saturated with potassium iodide or thiocyanate do not set at all at 10° C., and what comes to the same thing, gelatin disperses in these salt solutions even in the cold. A parallel effect on the viscosity has also been observed, inasmuch as the salts which raise the setting point increase the viscosity at a given temperature, and *vice versa*. Certain non-electrolytes also raise the setting point, etc., among which substances containing a large number of

hydroxyl groups are conspicuous, *e.g.*, several sugars. The effect of the cations of neutral salts is less well marked, but a certain order is also observable. We shall find parallel effects on the physical properties of gelatin gels, and on albumin sols, where the anion series will receive detailed treatment.

The optical properties of gelatin sols have received some attention. The refractive index has been studied by G. S. Walpole, who finds it to be a linear function of the concentration for a given temperature; since the hysteresis range of setting amounts to several degrees, it is possible to determine the refractive index of sol and gel at the same temperature, and the two values are found to be the same.

Gelatin sols are optically active and show to a very striking degree the phenomenon of multirotation, *i.e.*, the specific rotation increases with the age of the sol, a maximum being reached only after a few days. If the sol or gel is warmed, the rotation falls again to something like the original value.

Prolonged heating of a gelatin sol produces a profound change which shows itself on cooling, when the transformed sol no longer sets to a jelly. The product of transformation is known as β-gelatin or gelatose; since small amounts of it are formed even during short exposure to high temperatures, varying quantities of it are always present in gelatin and have some effect on its properties.

CHAPTER XIII.

A BEHAVIOUR differing entirely from that of gelatin is shown by the albumins, which are perhaps the most important among the organic emulsoids, and have received an amount of study commensurate with their importance. Within the limits of the present work it is impossible to give more than a mere outline of the principal properties of one type. As such we may take neutral albumin prepared from white of egg. The latter contains, in addition to albumin, other proteins, viz., globulin and ovomucoid which are precipitated by the addition of sufficient ammonium sulphate to produce a half-saturated solution. The clear liquid remaining after removal of the precipitate contains the albumin: the ammonium sulphate is removed by prolonged dialysis, when a sol of almost pure albumin is left in the dialyser. Some of the earlier investigations, however, were carried out with the whole white of egg, *i.e.*, a mixture of albumin and the other proteins: the procedure of Hofmeister (see below) consisted in beating the white to a froth, allowing this to stand in a tall cylinder, and collecting the clear liquid which separates from a fibrous coagulum.

Egg albumin disperses in water at ordinary temperature to form a slightly opalescent sol, which does not form a gel either with increasing concentration, nor on cooling or ageing. On the other hand, it shows a specific phenomenon: it coagulates irreversibly on heating to about 60° C. The heat coagulation has been studied extensively, especially

by Chick and Martin among others, and consists essentially of some chemical change followed by coagulation or aggregation. The second step may be prevented by suitable agencies ; if a well-dialysed albumin sol containing a thiocyanate is heated above the coagulation temperature no change can be observed, but has nevertheless taken place, as the albumin is precipitated when the salt is removed by dialysis, *i.e.*, the thiocyanate prevents the aggregation of the altered albumin particles but not their transformation. Other salts also affect the temperature at which heat coagulation occurs.

In close connection with this property of the albumin sol is its behaviour to salts in the cold. On the addition of salts in suitable concentrations the sol becomes turbid and the albumin finally settles out in flocculent masses. The coagulum, however, shows different characteristics with different salts, and these, if for the moment we consider only the cation, divide themselves into three groups. The salts of the alkalies and of magnesium produce coagulation or " salting out " only in great concentrations, and the process is *reversible ;* on dilution or removal of the salt, say by dialysis, the albumin again disperses. The salts of the alkaline earths salt out in similar concentrations, but the precipitate becomes insoluble on standing even for a short time. The salts of the heavy metals finally salt out *irreversibly* even in low concentrations, but show a further peculiarity : if the concentration of salt is increased beyond that necessary for precipitation, the coagulum disperses again, and this zone of redispersion may be followed, if the salt concentration is increased still further, by a second zone of coagulation. Thus zinc salts precipitate a 10 per cent. albumin sol in concentrations from N/1,000 to N/2 ; at this concentration the coagulum redissolves and remains so until the concentration reaches 4N, when a second precipita-

tion occurs. The coagulum always contains the metal, but in very variable proportions.

If we now consider, instead of a variety of salts with different cations, a series having the same cation—K· or Na·—we become acquainted with a series of the greatest importance, which was first discovered by Hofmeister, and is generally called after him. Some of his results are given in the following table, which shows the concentration in moles per litre of the sodium salts of various acids necessary to salt out the same albumin at 30° to 40° C.:—

Citrate	0·56
Tartrate	0·78
Sulphate	0·80
Acetate	1·69
Chloride	3·62
Nitrate	5·42
Chlorate	5·52
Iodide	Do not salt out in saturated solution.
Thiocyanate	

Hofmeister's experiments were made with albumin containing the other proteins of white of egg. The effect is roughly the same on pure albumin sols. A further striking property has been demonstrated by Pauli; the effect of the series is reversed in slightly acid sols, in which iodide and thiocyanate have the greatest, and citrates and tartrates the least action.

The preponderating effect of the anion on the coagulation—or other changes of state, such as gel formation—in other emulsoids has been referred to already. A chemical action seems out of question when we bear in mind that, as far as a parallel is possible, the anions act in a similar way not only on gelatin, which is a protein, but on substances as dissimilar as agar and even silicic acid. In addition to this, the anions arrange themselves more or less

exactly in the order found by Hofmeister, if their influence on a number of other phenomena is studied, *e g.*, on the surface tension and compressibility of water, on the solubility of other substances, on the inversion of cane sugar and the saponification of esters. With the latter processes we even find the inversion of the series according to the reaction—acid or alkaline—of the medium.

Freundlich, who has pointed out the connection between these various effects, calls them "lyotropic," and suggests that they are brought about by the neutral salt affecting the state of molecular aggregation of the water, and consequently the degree of hydration of solutes and disperse phases. The explanation is the most acceptable one which we have at present, and the generality of the lyotropic effect makes it eminently probable that it is due to alterations in the properties of the solvent or dispersion medium. We shall encounter it once more when discussing the properties of elastic gels, which are profoundly affected by the anions of the lyotropic series.

The action of acids and alkalies on albumin, and on proteins generally, is extremely complicated, and can only be touched on briefly. These substances are amphoteric electrolytes, *i.e.*, they behave as weak bases towards acids, and as weak acids towards bases. Protein salts are thus formed with either, which dissociate into protein cations and the anion of the acid, or protein anions and the cation of the base. With increasing acid or alkali concentration the protein undergoes gradual and irreversible chemical changes, which are more marked in the case of alkalies. In accordance with the above statement, albumin in acid medium is positively charged and travels to the cathode, while in alkaline medium it is negative and travels to the anode. The electric neutrality of albumin freed as far as possible

from electrolytes by very prolonged dialysis was first demonstrated by Pauli. He submitted the purified sol to electrophoresis in three small beakers connected by syphons, the electrodes being immersed in the two outside beakers. After the sol had been exposed to the electric field for a time, the albumin concentration in the beakers was determined, *e.g.*, by nitrogen determination by the Kjeldahl method.

The hydration of the disperse phase, and the stability and viscosity of the albumin sol are intimately connected with the degree of dissociation. In acid-albumin mixtures the stability and viscosity reach a maximum when the ionization is at a maximum ; both are at a minimum at the iso-electric point.

As salts of a weak acid or a weak base the protein salts also undergo hydrolysis. If albumin is treated with acid in low concentration for a short time and at low temperature, the latter can be removed again by dialysis, leaving the albumin unaltered ; the acid thus removed is no doubt liberated by hydrolysis, as in the dialysis of the nitrates of tri- or quadrivalent metals (see p. 68). It will readily be realized how complicated are the conditions in albumin sols containing acids or bases, and readers interested in this part of the subject must be referred to the large literature on the subject, more especially to Pauli's "Colloid Chemistry of the Proteins" (London, J. and A. Churchill).

Other proteins can receive only brief mention. Among them are the globulins, already referred to ; they do not disperse in water, but only in salt solutions of low concentration, *e.g.*, 0·7 per cent. NaCl. They accordingly precipitate when white of egg or serum is dialysed against water, as the salts present in both —which hold the globulins in dispersion—are removed. The process shows considerable hysteresis, so that the clear dialysate filtered off from the preci-

pitate which forms in the dialyser becomes turbid and deposits further globulin on standing.

Casein is produced from caseinogen, which is the most important protein constituent of milk, by coagulation with acid or rennet. Casein does not dissolve in water or in neutral salt solutions, but does so in alkali, forming a well-defined alkali caseinate. The solution of the latter is not coagulated by heating. It shows all the properties of a typical emulsoid sol, more particularly the rapid rise of viscosity with concentration, and the high temperature coefficient.

CHAPTER XIV.

A NUMBER of emulsoid sols with water, aqueou solutions and organic liquids as dispersion media, ca receive brief description only. Starch does no disperse in cold water, but above a certain tempera ture the granules burst and a bluish opalescent sol i formed; in a more concentrated condition it is know to everybody as starch paste. One of the mos striking characteristics of starch sols is their insta bility, which manifests itself, for instance, when th viscosity is determined several times in succession The later values are much lower than the earlier one the shearing undergone by the sol as it flows throug the viscometer being sufficient to alter its characte markedly. Separation of water also sets in rapidly this phenomenon is specially marked with highe concentrations.

Dextrin, another carbohydrate, forms sols in col water, and has a slight but perceptible protectiv action (see p. 63). Gum-arabic exhibits simila properties; it disperses in cold water without previou swelling, but if the temperature is kept near 0° C. period of swelling can be seen to precede dispersion Gum-arabic can be "salted out" reversibly by hig concentrations of neutral salts, the process bein evidently merely a withdrawal of water.

Among the carbohydrates which do not dispers in water alone, but in fairly concentrated solution of various electrolytes, the most important is cellu lose. It is dispersed by solutions of cupric oxid in ammonia (Schweizer's reagent), 50 per cent. solu tion of zinc chloride, and, as has been shown b

v. Weimarn, in concentrated solutions of a number of highly soluble and hygroscopic salts, *e.g.*, thiocyanate, at various temperatures and pressures. The cuprammonium sol is one of the materials for the manufacture of artificial silk, a coherent mass of cellulose being left behind if the dispersion medium is removed.

As regards sols in organic media, the esters of cellulose, and more particularly the nitrates and acetates, are of great technical importance. Some of the former dispersed in glacial acetic acid and in mixtures of ether and alcohol to form highly viscous sols known as "collodion," to which reference has already been made. Neither ether nor alcohol alone produces dispersion, and the problem of the "mixed solvent," which has no exact parallel with aqueous dispersion media, is very curious and deserving of further study. Cellulose acetate dispersed in various organic liquids plays an important part as "dope" for impregnating the wings of aeroplanes.

India-rubber forms sols with a number of organic solvents, such as benzene, petroleum ether, carbon tetrachloride, etc. They all exhibit high viscosity, though this differs, for equal concentrations of the same rubber, with different solvents—a remark which also applies to the cellulose esters.

The non-aqueous sols have so far received very little theoretical study, and the results of their technical examination are not accessible. The property most investigated so far is the viscosity, as the measurement of this constant is simple, and as experience has shown an intimate—if theoretically quite obscure—connection between the viscosity of a sol and certain properties of the disperse phase in bulk. Thus there is a distinct parallel between the viscosity of rubber sols, made under comparable conditions, and the elastic constants of the rubber. In the case of cellulose, there is a very remarkable persistence of some characteristics even when the

cellulose has undergone such drastic treatment as nitration. It has recently been shown (R. A. Punter, *Jl. Soc. Chem. Ind.*, *39*, 333T, 1920) that the viscosities of sols of various celluloses in cuprammonium solutions, and the viscosities of sols of the nitrates made from them, exhibit a complete parallelism.

The non-aqueous emulsoids and their gels still form a very promising field for research, and it may be added that hardly any of them have been submitted to the crucial test of dialysis, so that the evidence of their colloidal character rests on inferences which, though no doubt correct in many cases, are not conclusive in all. There is, of course, no difficulty in applying this test, given a membrane of which it has been definitely proved that it is permeable to the dispersion medium and that it retains particles of known size within the colloidal range. Ostwald and Wolski have recently shown that such membranes can easily be prepared for 97 per cent. alcohol, which retain mercuric sulphide (*Gen. Disc. Faraday Soc.*, October, 1920). They note the somewhat surprising result that the alcoholic solutions, *e.g.*, of resins, organic acids of high molecular weight, etc., all show perceptible diffusion through a membrane of this character. The extension of these investigations to other dispersion media is very desirable.

CHAPTER XV.

AFTER this brief description of individual emulsoids it is now possible to discuss the general characteristics of emulsoid sols. As regards their optical properties, they are either clear or slightly opalescent liquids, most of which show a Tyndall cone: the turbidity of the latter depends on the concentration, but also on the age and temperature of the sol (gelatin or starch sols). The ultra-microscopic image is much less striking than that of suspensoid sols; in general an amicroscopic light cone only is visible, but between certain limits of concentration (gelatin) submicrons become visible. The absence of submicrons, however, does not mean that the sols are homogeneous or contain particles of *amicroscopic size only*: it is much more probable that the disperse phase is invisible because it is not sufficiently differentiated *optically* from the dispersion medium, *i.e.*, the refractive index of the highly-hydrated particles may not be very different from that of the surrounding liquid.

Reference has already been made several times to the viscosity of emulsoid sols. This increases much more rapidly than the weight of disperse phase, and the temperature coefficient of viscosity is considerably greater than that of the pure dispersion medium. The two features are well illustrated in the curves A and B, Fig. 10, which represent determinations made by Chick and Martin on a sodium caseinate sol. In A the abscissæ are concentrations in per cent., while the ordinates are relative viscosities, that of the dispersion medium at the same

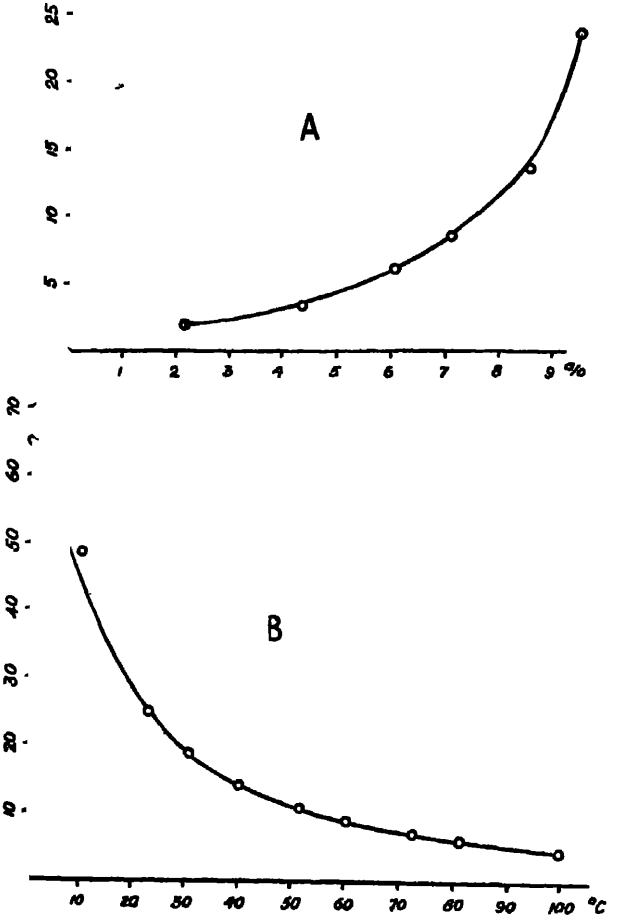


FIG. 10.—VISCOSITY OF SODIUM CASEINATE SOLS.

temperature being taken as unity; in B the abscissæ are temperatures, and the ordinates again relative viscosities, referred to water *at the same temperatures.*

The latter curve would of course become a horizontal straight line if the temperature coefficient of the sol and of water were the same. Fig. 11 shows viscosity—concentration curves after Schidrowitz and Goldsbrough for rubber sols: the enormous increase

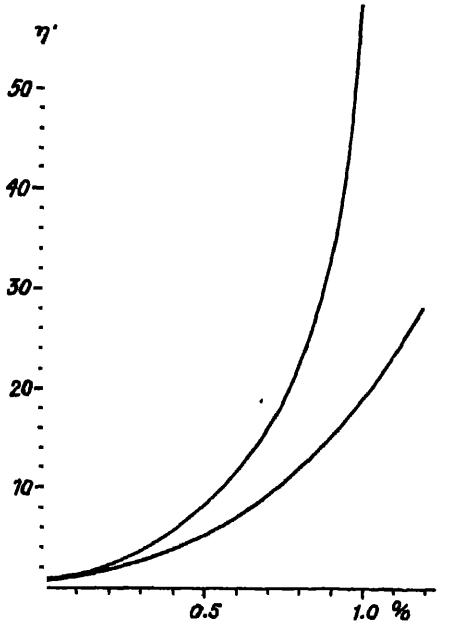


FIG. 11.—VISCOSITY OF INDIA RUBBER SOLS.

caused by concentrations as low as 1 per cent. is well shown by these examples.

The viscosity is not only markedly high for comparatively low concentrations, but exhibits anomalies absent in homogeneous liquids with high viscosity, such as glycerin or castor oil. It not only varies with the previous history, and the age of the

sol (silicic acid, gelatin), but is to a marked ext dependent on the rate at which the sol is shea These anomalies show themselves even in capillary viscometer, but are more easily stuc with other apparatus which permits a ready va tion of the rate of shear. The first quantitat investigations were carried out by Garrett, v employed the method of measuring the logarith decrement of a disc oscillating in its own plane the liquid, from which the viscosity can be dedu by calculation. He found that the viscosity va with the amplitude of oscillation, that it increa rapidly with continued shearing, etc. The cor tions with the oscillating disc are too complica to permit interpretation; another method, that measuring the deflection of cylinder suspen coaxially in a cylindrical vessel filled with the liq and rotated with uniform velocity, is free from t defect, and has been employed by the auth Fig. 12 shows the results obtained with the sa gelatin sol, A, 48 and B, 24 hours old: the absci are rates of shear (which are simply proportional the speed of rotation) in arbitrary units, while ordinates are the viscosities. The viscosity *decrea* rapidly with increasing rate of shear, and that of sol 48 hours old is throughout much higher than viscosity at 24 hours, a change referred to already p. 83. The results are strong evidence of the t phase character of these sols, and differ strikin from those obtained with homogeneous liqui the viscosity of water, *e.g.*, has been shown by v careful experiments to be independent of the r of shear over the whole range here used.

The osmotic pressure of some protein sols has b studied by Lillie, Moore and Roaf, Bayliss and othe Appreciable osmotic pressures have been obser *e.g.*, 22·4 mm. of mercury for a 1·25 per cent. albun sol, 6·2 mm. for a 1·5 per cent. gelatin sol, etc. T

pressure shows marked hysteresis phenomena, thus on heating it increases more rapidly than that of true solutions, and on cooling does not return to the

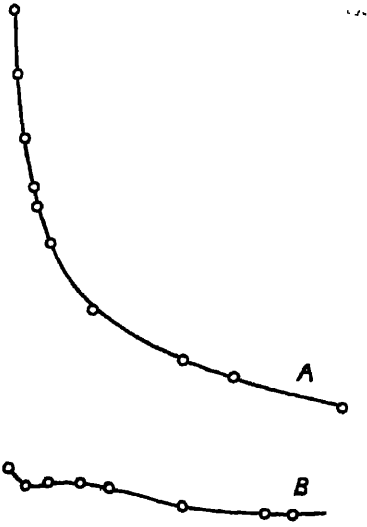


FIG. 12.—VARIATION OF VISCOSITY WITH RATE OF SHEAR.

initial value for a very considerable time. Electrolytes affect it markedly; in studying their action the pressure due to the electrolytes itself has to be balanced by providing the same concentration outside the semipermeable membrane as inside it. Acid and alkali in these conditions cause a very large

increase in the osmotic pressure of proteins, no doubt due to the formation of dissociating protein salts.

As has been mentioned repeatedly, all the properties of many emulsoid sols undergo changes with time, even if conditions are kept constant. The property most conveniently measured and therefore most extensively investigated is the viscosity. In most sols, *e.g.*, silicic acid or gelatin, the viscosity coefficient increases with age, and this increase is ascribed to growing hydration or increasing size of the aggregates of disperse phase. The latter process undoubtedly occurs in the early stages of the dialysis of reaction mixtures of silicic acid, since the acid passes copiously through the membrane at that period (p. 78). In other cases the viscosity decreases with age; a notable instance is the ceric hydroxide sol, which on keeping gradually loses its property of setting to a gel on addition of electrolytes, a change which may on good grounds be ascribed to progressive dehydration. Rubber sols exposed to light have been found by several observers to decrease in viscosity; the cause suggested—perhaps on insufficient evidence—is "depolymerization."

The electrical properties differ too much in individual sols to allow of any general summary. The charge on the disperse phase is in all cases intimately connected with the degree of hydration, and its removal affects the system largely, if not entirely, through the change in hydration.

CHAPTER XVI.

We have now to consider a number of substances showing peculiarities differing markedly from those of the more typical emulsoids described so far, and forming a more or less gradual transition to true solutes. Among these the soaps, more particularly the sodium and potassium salts of the fatty acids, take the first place as regards theoretical interest and technical importance. Our knowledge of the soaps rests to a great extent on the exhaustive investigations of McBain and his pupils.

In alcohol the soaps form true solutions showing the general characteristics of solutions of a simple and rather weak electrolyte. In water they exhibit a marked anomaly, inasmuch as they possess the conductivity of a moderately strong electrolyte but an osmotic pressure very much lower than would account for this conductivity. The deficiency in osmotic pressure must be ascribed to the formation, from a portion of the dissolved soap, of colloidal particles or aggregates too large to exert an appreciable osmotic pressure; that measured is practically due to K or Na ion only. The conductivity, however, is much greater than corresponds to this cation concentration, and to reconcile this discrepancy it is necessary to assume that the colloidal particles carry each a large number of charges so that their mobility becomes that of an ordinary ion in spite of their large size. The constitution which McBain finally ascribes to these colloidal anions is that they are aggregates

of undissociated soap molecules, a number of fatty acid anions and a—probably large—number of water molecules. The reader will be struck by the analogy with proteins (p. 90).

In other respects soap solutions exhibit fairly marked emulsoid behaviour; on cooling or on the addition of salts they set to clear gels or to opaque masses which McBain differentiates from the former as "curds." They are also "salted out" by high concentrations.

The dyestuffs exhibit a very great variety of behaviour. Some, like eosin or methylene blue, are in true solution, show no heterogeneity in the ultramicroscope and diffuse rapidly. Others, like Congo Red, and even more strikingly Congo Rubin, which latter has been studied in great detail by Wo. Ostwald, behave almost like typical suspensoids. Both are sodium salts of a blue acid and, therefore, turn blue on the addition of free acid. Congo Rubin also turns violet or blue on the addition of neutral salts and even of $Ba(OH)_2$ and eventually precipitates as a purple or blue coagulum, very much like a gold sol. The effect of the valency of the cation is quite marked; with many electrolytes in suitable concentrations the colour change is reversible by mere heating, *i.e.*, the purple sol turns red and remains so on cooling. Congo Rubin sol can be protected by the same emulsoids as gold sol, although the order is not quite the same; it exhibits the further striking peculiarity that protection may be effected *after* the colour change has taken place (see p. 65). On the addition of protective colloid to a sol turned purple by electrolyte the colour changes back to, and remains, red.

The osmotic pressure of the related Congo Red has been investigated by Bayliss. This dye does not diffuse through parchment and behaves towards electrolytes like a negatively charged suspensoid;

nevertheless the sol has an osmotic pressure only slightly less than that calculated from the (simple) formula weight and is a good conductor in high dilution. The blue dye acid, on the contrary, has an abnormally low osmotic pressure.

Night Blue, on the other hand, is positively charged and recalls the hydroxide sols in showing some emulsoid characteristics. Concentrated solutions are viscous, and the viscosity varies with age and with the concentration of electrolytes present. It is hardly necessary to add that dye sols with opposite electric charges precipitate each other, and that the phenomenon agrees with the rule given above (p. 62), viz., precipitation is complete when the two sols are mixed in certain ratios, but does not occur if either is in excess.

Many dyes which are optically void in the ultramicroscope show particles after the addition of neutral salts (Fuchsin with NaCl) or more frequently of acid or alkali, the dye acid or dye base liberated being colloidal while the dye itself is not. A very exhaustive ultra-microscopic investigation of fifty dyes of the indicator class has been carried out by Wo. Ostwald, from which it appears that in practically all cases either the base or the acid, if not the dye itself, shows particles or at least a diffuse light cone.

In alcohol or other organic solvents many dyes show true solubility and exhibit normal osmotic pressure and molecular weight.

A number of substances, frequently described as " semi-colloids " provide a gradual transition to true solutions. Among them are the various products of cleavage of proteins. Protalbic and lysalbic acid, for instance (see p. 64), show a measurable depression of the freezing point, and the latter diffuses perceptibly through parchment; on the other hand, their solutions and those of their alkali salts are turbid

and become viscous in high concentrations. Peptone solutions behave similarly, and the chief properties which link them to the emulsoids are slight turbidity and the syrup consistence which they assume with increasing concentration.

CHAPTER XVII.

REFERENCE has already been made in several of the preceding chapters to the changes which sols like those of gelatin and agar undergo on cooling, or which take place in silicic acid sol on ageing or on the addition of electrolytes. The sols in these conditions set to coherent gels without—at any rate immediate—loss of dispersion medium, and notwithstanding the very large amount of the latter present in some of them—2 per cent. agar makes a very stiff gel—they possess some of the properties of solids. The term "gel" was applied by Graham to all the products of transformation of sols, but in the following is restricted to such as have been quoted above and similar systems, in which no appreciable segregation of the phases takes place. It may be well to mention here that, even in its restricted meaning, the term is not capable of strict definition: by the majority of authors it is applied to transparent or opalescent masses containing a large percentage of liquid which retain their shape, offer some resistance to mechanical deformation and show no microscopic structure.

The gels are generally divided into "elastic" and "rigid" gels. Gelatin, agar, the rubber and cellulose nitrate gels belong to the former class, while silicic acid gel is the principal representative of the latter. The distinction is not altogether happy, since a moderately concentrated silicic acid gel can be felt to vibrate when the vessel containing it is struck, but they are descriptive of some properties which will be understood when the individual examples have been described.

Silicic acid is the only rigid gel which has been studied exhaustively. It is obtained in its pure form by allowing a well dialyzed sol to set, either spontaneously or by small additions of ammonia, a carbonate or a phosphate. The sol becomes bluish and sets to a jelly, the opalescence of which increases for some time after setting is apparently complete, *i.e.*, after the vessel containing the gel can be turned upside down. No appreciable segregation of water occurs immediately nor, if the gel is dilute, even after some time. With concentrated gels, however (5 per cent. SiO_2 or more), a very striking change shows itself within a few minutes. The gel, which appears perfectly dry immediately on setting, becomes covered with drops of liquid which rapidly increase in size, and at the same time liquid is exuded between the gel and the walls of the vessel. After twenty or thirty minutes this has progressed so far that the gel will slip out of the containing vessel when this is inverted. This segregation of liquid—which also occurs in all the elastic gels in suitable concentrations—had already been observed by Graham, who called it "Syneresis"; it is a phenomenon probably of great importance in nature which deserves more study than it has received up to the present.

The pure gel, if left in air, rapidly loses water, even at ordinary temperature, and dries to a glass-like transparent mass which is not opalescent. It still retains several moles of water per mole of SiO_2, which can be removed by drying over sulphuric acid. The course of dehydration has been studied by van Bemmelen in a series of classical investigations, prolonged in one instance for two years. The gels were kept in desiccators containing sulphuric acid-water mixtures of known vapour pressures and were weighed at frequent intervals. By passing the dry gel through the series of desiccators in the inverse order the course of rehydration was likewise

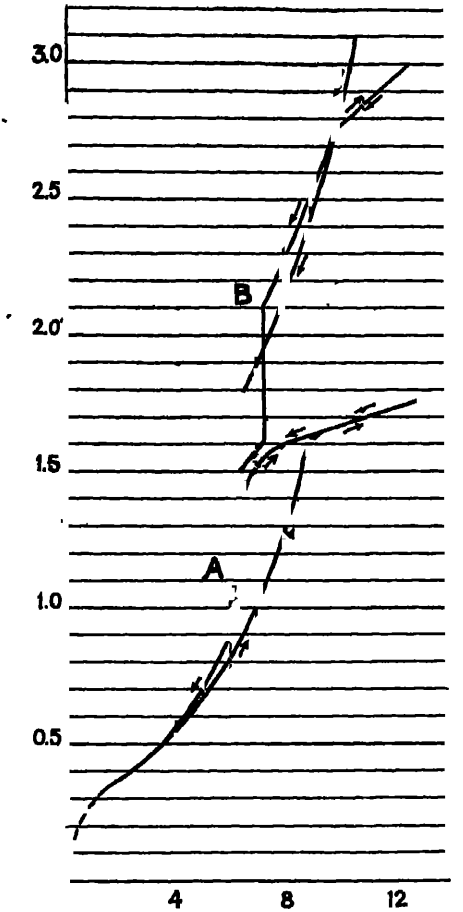


FIG. 13.—DEHYDRATION OF SILICIC ACID GEL.

investigated. The results, covering the range from 3 to 0 moles of H_2O per mole of SiO_2, are plotted in Fig. 13, in which the abscissæ are the vapour

pressures in millimetres of mercury, the ordinates the water concentration in moles, and the arrows indicate the direction of the process, viz., those pointing towards the left dehydration, and those pointing towards the right rehydration.

The first point to be gathered from the examination of the diagram is that there are no definite hydrates, but a continuous loss of water with an equilibrium corresponding to every given vapour pressure. In this respect the gel differs radically from crystals with water of crystallization. Copper sulphate, *e.g.*, crystallizes with five molecules of water, four of which are given off at 100° C. and the fifth at 200°. A dehydration curve plotted with the temperatures as abscissæ and the water contents as ordinates would therefore be discontinuous and would consist of a succession of straight lines.

We meet here, for the first time, a class of compounds quite definite under given conditions, but in which the ratio of the constituents can change *continuously* and not only by steps corresponding to simple stoichiometric ratios. We shall have an opportunity of considering such systems in connection with the laws of absorption.

The gel undergoes a very striking change, which must be mentioned specially, as throwing light on the structure of the dry gel. At A the gel is transparent, while at B it becomes white and opaque, somewhat resembling porcelain. On still further drying, however, the gel becomes clear again and is transparent in the last part.

The process of dehydration is reversible in parts, but rehydration shows hysteresis. The curves branching off to the right at 2·75 and 0·5 moles show, according to the arrows, the course of *rehydration* begun at those points, and of a second dehydration.

The completely dried gel imbibes organic liquids and remains clear. If placed in water or even a

moist atmosphere, it begins to crack violently and disintegrates into small fragments. Investigations to elucidate its structure have been carried out, principally by Zsigmondy and his pupils Bachmann and Anderson, with the following results :—

Since the gel rapidly imbibes liquid, it must be porous and the pores must communicate in all directions. A limit to the size of the pores as well as to the thickness of the walls between them is fixed by optical considerations; since the gel, whether filled with air or with an organic liquid, is transparent except at B, both the dimensions mentioned must be small compared with the wave length of light, as otherwise, in consequence of the difference in refractive index of walls and contents, the whole would appear turbid. The actual size of the pores can be calculated with a reasonable degree of approximation from the vapour pressure of the liquid contained in the gel. As is well known (see " Surface Tension and Surface Energy ") the vapour pressure over the concave meniscus formed by a wetting liquid in a capillary is *lower* than that over a plane surface of the same liquid, and the radius of the capillary can be calculated from the two vapour pressures. The value thus arrived at is about 3 $\mu\mu$. While the gel is transparent when *filled* either with liquid or with air, the formation of any spaces containing air in a gel still largely filled with liquid would cause an optical heterogeneity sufficient to produce turbidity, and this is Zsigmondy's explanation of the sudden opacity shown at the point B of the dehydration curve.

The structure of the fresh silicic acid gel cannot be determined by such methods and is still a matter of controversy, to which it will be more convenient to refer when elastic gels have been described. Examination by X-ray interference, carried out by Scherrer (R. Zsigmondy, " Kolloidchemie," 3rd

edition, 1920, p. 407) has not revealed any trace of crystalline structure, although this shows itself in dry and particularly in ignited gels.

Another gel of the same type which has, however, received very little attention is that of ceric hydroxide (see p. 68). It is a pale yellow and, according to the extent to which it has been dialyzed, and to the rapidity of coagulation, either quite clear or opalescent. It dries to a reddish brown translucent mass at moderate temperatures, but the change has not been investigated in detail. The fresh gel is remarkable for the ease with which it can be peptized again; contact with fresh sol or the addition of 1 or 2 drops of N/1 nitric acid are sufficient to transform the gel back into sol after a few hours.

Another rigid gel which deserves further study is that of gelatin hardened with formaldehyde. If an ordinary gelatin gel is exposed to formaldehyde gas or submerged in the aqueous solution, it gradually becomes much harder, very brittle and dries to a friable mass. The gel so treated, unlike the natural gelatin gel, no longer swells in water. Prolonged submersion in water which is changed at intervals removes the greater part of the formaldehyde and the gel reverts more or less completely to its original condition.

Diffusion and reactions in rigid gels, more especially in silicic acid gel, have not received as much attention as the same phenomena in elastic gels, and will receive mention when the latter are described.

CHAPTER XVIII.

THE typical representative of the elastic gels is that of gelatin, which has been studied in various aspects by a large number of observers. The raw material or dry gel occurs in commerce in sheets (generally showing the diamond-shaped markings of the wire netting on which they have been dried), as powder and in the form of thin shreds. The air-dry material contains, in ordinary atmospheric conditions, from 10 to 15 per cent. of water, most of which can be removed by drying at 100° C. If the dry gel is placed in an atmosphere saturated with moisture, it takes up water, rapidly at first and then more slowly, until equilibrium is attained. In an experiment by Schroeder the weight of water thus taken up by a gelatin plate weighing dry 0·904 gm. was 0·37 gm. after eight days, after which it remained constant. The plate was then submerged in water at the same temperature and took up a further 5·63 gm. in the first hour. The process is accompanied by a considerable increase in the volume of the gel—a change which in the absence of a special term is usually described as " swelling "—and the process continues for a considerable time, which depends on the linear dimensions of the piece investigated. At a given temperature equilibrium is finally reached.

If the fully swollen gel is now placed in a dry atmosphere, it rapidly loses water with a corresponding decrease in volume. A great portion of the water is held quite loosely, and evaporation from the gel proceeds at first as rapidly as from a water surface of the same area (Pauli). An equilibrium

determined by the vapour pressure is finally attained in drying.

While the gel imbibing water swells, the total volume, gel plus water, *decreases*, *i.e.*, the process is accompanied by compression, as occurs, of course, also in many cases of true solution. While the compression is easily demonstrated qualitatively, it has hardly been investigated quantitatively and work in this direction would be of great interest. At present it is not even possible to say which of the components, if not both, undergoes compression, though the effect of the lyotropic series of anions, which will be described shortly, makes it probable that the water is responsible for at least part of it. In any case it follows from compression taking place in either phase that the process of swelling must be accompanied by the liberation of heat. This is indeed the case, and calorimetric measurements have been made on gelatin as well as on other substances which, like it, swell in water. The following figures are given by Wiedemann and Luedeking :—

Gel.	Heat developed on swelling, in gramme-calories per gm. of gel.
Gelatin	5·7
Starch	6·6
Gum-arabic	9·0
Gum-tragacanth	10·3

While the total volume, gel + water, decreases, that of gel + imbibed water increases and the gel swells. The swelling can be demonstrated and measured with some degree of accuracy in a variety of ways. One method consists in placing in test tubes of equal diameter weighed amounts of the powdered gel, adding the dispersion medium and measuring the increase in height of the layer of gel. With gelatin another method may be used. Circular discs are cut from a gelatin sheet or foil of uniform

thickness and submerged in the liquids to be examined; as the discs swell in all three dimensions, the volume increases with the *cube* of radius, which is most conveniently measured.

It is well known that gels, and the complicated organic tissues composed of them, exert considerable forces when swelling. To measure these it is, of course, necessary to confine the gel in such a way that the water has access to it, but is not implicated in the volume changes. An apparatus in which this is possible was designed by Reinke and called by him "Œdometer": a diagrammatic section is shown in Fig. 14. He examined, not a simple gel, but dry discs of *Laminaria*, a sea weed. These were placed in the cylinder A, which they fitted exactly, and weighted by a piston provided with numerous fine perforations, through which water contained in the upper part of the cylinder could reach the discs freely. As the latter could expand only axially the increase in volume was simply proportional to the linear displacement of the piston. The table on page 114 gives the pressure on the piston in atmospheres (kilogramme per square centimetre) and the percentage increase in volume which the imbibition of water produces.

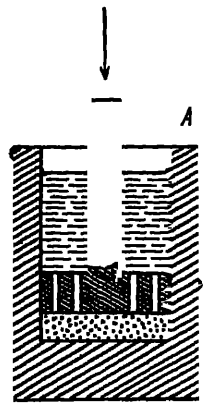


FIG. 14. — DIAGRAMMATIC SECTION OF ŒDOMETER.

This table also illustrates strikingly the large amounts of energy that enter into the process. Even against the enormous pressure of over 41 atmospheres the gel still expands 16 per cent., while with a pressure of 1 atmosphere the expansion amounts to 330

per cent. In other words, if a cube of gel having an edge of 1 cm. is allowed to swell in one dimension only (as in the œdometer) to saturation, it will lift 1 kg. 3·3 cm. Conversely it becomes clear what enormous pressures are necessary to remove the last traces of water from a gel, as the present example still retains 16 per cent. under a pressure of 41 atmospheres.

The process of swelling is naturally controlled by the diffusion of the liquid to, and into, the gel, and this dependence becomes marked if larger bodies of gel are allowed to swell. The outer layers in imme-

Pressure in atm.	Percentage increase of volume.
41·2	16
31·2	23
21·2	35
11·2	89
7·2	97
3·2	205
1·2	318
1·0	330

diate contact with liquid swell rapidly; to reach the interior, the liquid has to diffuse through an increasing thickness of swollen gel and reaches a gradually decreasing volume of dry gel. The sum of these effects is that the increase in weight becomes slower with time. A body of gel, unless it is of a simple shape with more or less uniform radius of curvature, does not remain similar to itself during swelling, and may undergo very considerable distortion if its shape gives very unequal facility for diffusion, *i.e.*, if it has points, edges, or portions differing greatly in thickness.

The drying of a gel is the converse and is controlled by the diffusion of the liquid through the gel to the surface. Edges or points dry more rapidly than the

rest, contract and eventually become much more rigid than larger surfaces, in which drying proceeds more slowly. This again may lead to considerable distortion. An illustration is given in Fig. 15, which gives diagrammatic profiles of three stages in the drying of a cylinder of 10 per cent. gelatin gel.

The swelling of gelatin and of other gels is very considerably affected by substances dissolved in the water, and most strikingly by salts of the lyotropic series. In citrate, tartrate or sulphate solutions, the gel swells *less* than in pure water, while in iodides and thiocyanates swelling is considerably increased; in sufficiently concentrated solutions of the latter it

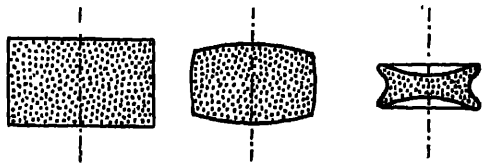


FIG. 15.—SUCCESSIVE STAGES IN DRYING OF GELATIN GEL CYLINDER.

disperses even *in the cold*. The action—as far as an analogy is possible—is parallel with that on sols (see p. 84); the anions which raise the viscosity and the setting point reduce the amount imbibed, while those which lower the viscosity and the setting temperature increase it. A similar effect on the elastic properties of the gel will be referred to shortly.

Gelatin gels show perfect elasticity under moderate stress applied for a short time. If the application is prolonged, the stress gradually disappears, *i.e.*, the gel relaxes and retains the shape to which it has been deformed. Determinations of the modulus of elasticity for tension have been made by various investigators. A table due to Leick is here given. C is the

gelatin concentration in per cent., E the modulus for tension in grammes per square millimetre.

C.	E (gm./mm.^{2}).	E/C^2.
10·0	2·42	2·4
18·6	9·78	2·8
30·0	15·45	1·7
45·0	29·44	1·5

For the lower concentrations the modulus is approximately proportional to the *square of the gelatin concentration*, as appears from the last column.

The gels do not attain their full strength immediately on setting, but the modulus increases for some time and does not attain its maximum value until three or four hours afterwards. The volume remains practically constant during deformation, a behaviour which is not surprising in view of the large amount of liquid contained in the gel. The influence of various solutes has also been studied; chlorides and nitrates lower the modulus markedly, while sulphates raise it slightly and cane sugar considerably. These effects again show the same order as the action of the same solutes on the setting points of sols and the swelling of gels.

Gels free from strain are isotropic, *i.e.*, they have the same coefficient of thermal expansion, modulus of elasticity and refractive index in all directions. The coefficient of expansion in these circumstances is practically, and over a fair range, that of the liquid contained in the gel. The refractive index is, like that of sols, a linear function of the gelatin concentration. If a gel is strained, it becomes birefringent; owing to the difference in the rate of setting in ordinary vessels, it is difficult, without considerable precautions, to obtain bodies of gel entirely free from strain. Uneven drying produces similar effects: if a small cube of 10 per cent. gelatin gel is observed with polarized light while drying at ordinary tem-

perature, the first signs of double refraction generally show within about five minutes, and the strain due to the shrinking of the edges is very marked after 20 or 30 minutes.

The properties of gels other than that of gelatin have so far received very little investigation, and the non-aqueous systems in particular would repay study. One phenomenon already described in connection with silicic acid gel—syneresis—is common also to elastic gels, though the concentration at which it is most marked differs considerably. While silicic acid gel shows marked syneresis at high concentrations, with gelatin and agar gels it is best observed in dilute gels. Agar gels containing 1 or 1·5 per cent. of the dry substance, on standing for a few hours segregate a perceptible quantity of liquid —a phenomenon well known in its bacteriological use as a culture medium. The syneretic liquid is in no case—including silicic acid—the pure dispersion medium, but always contains a small amount of disperse substance. If the dispersion medium is a solution, the solute is likewise found in the segregated liquid, but the concentrations in the latter and in the gel are generally different. Some gels in organic media, *e.g.*, viscose (cellulose xanthate) or india-rubber vulcanized in solution, show syneresis even more strikingly than do the aqueous gels ; in viscose the liquid segregated after some months may amount to 50 per cent. of the original volume.

The phenomenon has received singularly little attention since it was first observed by Graham, but in many of his recent publications Wo. Ostwald has insisted on its great theoretical importance and on its possible bearing on problems like that of secretion from glands, etc. This property of gels—as, indeed, most of them—still offers a large and promising field for research.

CHAPTER XIX.

THAT dissolved substances diffused into and out of gels was known already to Thomas Graham, and is a fact familiar to every photographer, as the various processes of developing, fixing and toning are made possible only by the diffusion of the respective solutions into the gelatin gel containing the silver salt. Graham also observed the difference in the behaviour of true and colloidal solutions—which latter do not diffuse perceptibly into gels—noticed that solutions of, *e.g.*, sodium chloride diffused in gelatin gel with almost the same velocity as in water alone, and made use of this observation to determine diffusion constants in gels, thus avoiding the difficulties caused in liquids by convection currents, etc.

The difference between true and colloidal solutions can be easily demonstrated by filling test tubes to about two-thirds of their height with 1 per cent. agar sol, allowing it to set and then pouring on the solutions to be examined. While solutions of, say, potassium dichromate, copper sulphate or some dyes like methyl violet will be found to advance rapidly into the gel, sols of gold, or of dyes like Night Blue, Congo Red, etc., will not penetrate into it.

Further investigation since Graham's time has shown that the rate of diffusion is unaffected only in dilute gels, but is materially slower in more concentrated gels than in the pure liquids. The permeability of gels to solutes can be altered, like all their other properties, by various dissolved substances. Without going into details it may be said that the study of diffusion is by no means simple:

even with strongly coloured solutions like those of dichromates it is not easy to fix the actual boundary, since there is a steady gradient to zero concentration. An indicator can be used only if it does not itself diffuse appreciably, as otherwise the results are vitiated by its movement in the opposite direction: dyes of the indicator type generally fulfil this condition. Another method consists in so arranging the body of gel—for example, cylinders cast in test tubes lined with parchment—that it can be examined over its entire surface: it is withdrawn at intervals and the extent of diffusion determined by "spotting" with a suitable reagent. Experiments of this description have been carried out by Bechhold and Ziegler, who found that the addition to a gelatin gel of sodium sulphate, glucose, alcohol or glycerin retarded diffusion, while urea, iodides and chlorides accelerated it. These effects are again parallel with the changes in setting point and elastic properties caused by the same solutes.

Since a solute will diffuse into a gel containing another substance in solution, it is possible to produce reactions in gels, and these are of very considerable interest, since the innumerable reactions which occur in organisms very largely proceed in media with the properties of gels. Two cases have to be distinguished: reactions producing one (or two) insoluble reaction products, and those in which all the products of the reaction are soluble. In the latter case, which has received comparatively little attention so far, diffusion takes place in both directions, *i.e.*, the solute contained in the gel diffuses into the aqueous solution, and *vice versâ, irrespective of the concentrations and osmotic pressures of the two reaction components.* If, for instance, a test tube is partly filled with agar gel containing copper sulphate, and a solution of ammonia poured on top of the gel, both the latter and the supernatant

aqueous solution turn deep blue owing to the formation of copper oxide-ammonia (S. C. Bradford, *Bioch. Jl.*, *14*, 474, 1920).

If one product of the reaction is insoluble, the case is different, and diffusion proceeds only from the component with *higher osmotic pressure to that with lower pressure.* If the solutions are isotonic, an extremely thin layer of precipitate is formed, and the reaction and diffusion do not proceed any further. This has been demonstrated by Bechhold and Ziegler with gelatin containing sodium chloride covered with a solution containing an equivalent (and isotonic) solution of silver nitrate. A barely visible film of silver chloride is formed and diffusion then ceases. They showed further that if the film of gelatin containing AgCl is melted and allowed to set again, the reaction proceeds once more, a result which will be referred to later.

The rule just stated that diffusion producing an insoluble reaction product proceeds only into the component of lower osmotic pressure was first formulated by Pringsheim, and is generally called after him. Exceptions occur where the rate of diffusion is very markedly different, and where one component has a strong lyotropic effect.

Whether the reaction proceeds in the aqueous solution or, which interests us more at the moment, in the gel, it is controlled by the rate of diffusion, and therefore, generally speaking, proceeds slowly, so that conditions are favourable to the formation of large crystals of the reaction product. The author and A. Simon were able to produce gold crystals up to 3 mm. across by reducing gold chloride in silicic acid gel with oxalic acid; Holmes obtained large tetrahedra of copper by reduction of copper salts with hydroxylamine, also in silicic acid gel (*Jl. Am. Chem. Soc.*, *40*, 1187, 1918), etc. In many cases the precipitate tends to form spherical aggregates, and

often perfect spherolites; earlier investigators like Harting obtained them with calcium salts, which are of particular interest in view of their deposition in the endo- or exo-skeletons of organisms. Since then very many compounds, like silver chromate, barium silicofluoride, manganese sulphide, etc., have been obtained by various workers. Fig. 16 is a photomicrograph between crossed nicols of sphero-



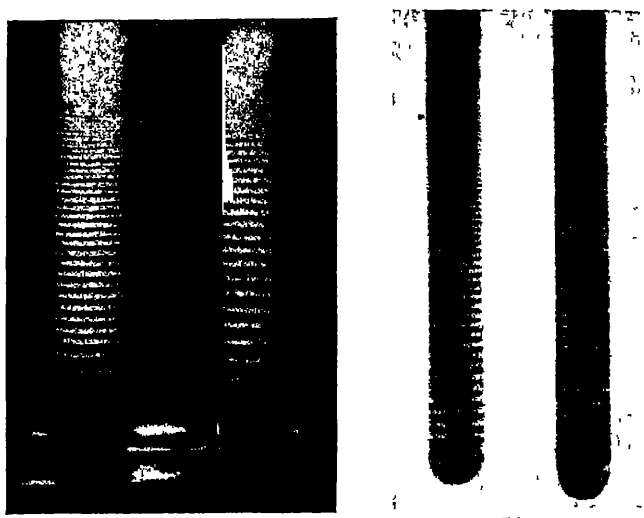
FIG 16. — SPHEROLITES OF $BaSiF_6$ BETWEEN CROSSED NICOLS.

lites of barium silicofluoride, showing the black cross and rings of several orders.

These results show that large aggregates of very insoluble substances can be formed by reactions in a gel in comparatively short times; they thus throw considerable light on many questions of physiology, pathology, and geology, detailed discussion of which is beyond the scope of this book.

A further phenomenon of very great interest was first observed by Liesegang, and is generally called

after him. The original experiment is made as follows: a drop of silver nitrate solution is placed on a film of gelatin gel containing a little potassium dichromate. The silver salt diffuses into the gel, and silver dichromate is precipitated which, however, is not deposited in a continuous zone round the drop,



(a) (b)

FIG. 17.—LIESEGANG STRATIFICATIONS. (a) CALCIUM PHOSPHATE IN GELATIN. (b) LEAD CHROMATE IN AGAR.

but in concentric rings separated by apparently clear intervals which increase in width towards the periphery. A number of other reactions have since been found to lead to the same result, and larger volumes can be dealt with by placing the gel in test tubes and pouring the aqueous solution on top. Fig. 17 shows such stratifications of (a) calcium phosphate in gelatin, and (b) lead chromate in agar obtained by

the author. In the former case a solution of calcium chloride diffused into the gel containing trisodium phosphate, in the latter a solution of sodium dichromate into an agar gel containing lead acetate.

The phenomenon is of very great interest for the following reason. Very many banded or stratified structures occur in both organic and inorganic natural products, and their explanations have so far involved assumptions like a periodic supply of one or both components, or a periodicity in external conditions like temperature. The Liesegang shows that very striking periodic structures may be formed when all the factors involved remain constant, or, at any rate, do not undergo periodic variations synchronous with the formation of strata.

The phenomenon is extraordinarily sensitive, in the first instance, to changes in the nature of the gel. Different brands of gelatin give widely differing results with a given reaction, if all other factors are kept constant, and a reaction which produces excellent stratifications in gelatin may fail to do so in agar, and *vice versâ*. Some of these divergences are undoubtedly due to the difference in the protective effect of the various gels, which tends to prevent the formation of excessively large crystals; the effect is very great in gelatin, slight in agar and almost negligible in silicic acid gels. In the last named the formation of strata is therefore comparatively rare, while that of large crystals is fairly common.

There is at present no generally received explanation of this very striking phenomenon. A theory was propounded by Wilhelm Ostwald soon after its discovery, based on the assumption that the reaction product at first remains in supersaturated solution, until the limit of "metastability" is reached, when it crystallizes out. The reaction product existing in a certain zone, and the component in the gel, are thus exhausted round the precipitate, and a further

stratum can form only when the metastable lin has again been reached; owing to the decreasi concentration the distances between successive rin increase.

Experiments published by the author show th stratifications can be obtained when the crystalli reaction product (PbI_2) is present throughout t gel, and also that a second system of strata can produced in a gel already containing one, althou in both cases supersaturation is impossible.

A promising theory has recently been advanc by S. C. Bradford and supported by experiment evidence (*Bioch. Jl.*, *11*, 14, 1918; *14*, 29, 192 *14*, 474, 1920). He suggests that the reacti product adsorbs the component present in the g so that a zone of some depth below the last layer precipitate is practically free from the latter, or, other words, the concentration is so low that t solubility product of the precipitate is not exceede The component in the aqueous solution must ther fore diffuse some distance again until this conditi is satisfied, *i.e.*, strata separated by clear interva will be formed. As adsorption (see Chapter XXI depends on the specific surface of the adsorbi material, its effect will not be marked unless t latter reaches a certain degree of dispersity, a Bradford has shown that, by increasing the latt systematically, a reaction which ordinarily fails produce stratifications (*e.g.*, silver chromate in aga can be made to yield them in great perfectio Further critical experiments are required before t theory can be held to be generally established, a the whole phenomenon offers a very attractive fie for investigation.

CHAPTER XX.

THE reader will have noticed that no attempt has, so far, been made to fit the gels into the classification of disperse systems given on p. 8. This omission is deliberate, as it is not possible to assign them a place *à priori*, and the only feasible procedure is to attempt to deduce their structure from the properties which have been briefly described in the preceding chapters.

As regards the *dried* rigid gels, like that of silicic acid, the case is comparatively simple. We have seen that these are porous masses in which the dimensions of both the pores and of the walls separating them are of amicroscopic order. The walls must be continuous to account for the coliesion of the gel, but the pores must also communicate very completely in view of the ready imbibition of liquids. We assume, therefore, a continuous solid and a continuous liquid or gaseous phase—a conception which offers no particular difficulty; we can imagine numerous macroscopic models, *e.g.*, an aggregate of polyhedral cells with perforated cell walls, etc. Substances like pumice stone or artificial porous materials, the pores of which can also be readily filled with liquid, are, no doubt, coarser systems of the same kind.

Gelatin gels hardened by various agents, *e.g.*, alcohol, behave like rigid gels, imbibe organic liquids and on drying show the same characteristic phenomena as silicic acid gel.

The difficulties become very much greater when we turn to the fresh silicic acid gel and to the elastic gels. The fundamental questions whether

these gels are homogeneous or heterogeneous system and, in the latter event, what are the geometric form and the state of aggregation of the phases, ar answered in opposite ways by different investigator

The view that gels are homogeneous systems i held—to name only its principal supporters—b Pauli, Katz, Procter and Loeb. Roughly speaking this view is based on the negative ground that n assumptions regarding structure are necessary t account for the observed properties of gels. Thu Katz, as the result of a very careful and exhaustiv study of swelling, arrives at the conclusion that i does not differ from other processes of solution, s that, *e.g.*, a gelatin gel is simply a solution of wate in gelatin. Procter arrives at a similar result largel through the investigation of the swelling of gelati in acid, the "uncomplicated" swelling in pure wate as well as similar phenomena in non-aqueous solvents being disregarded. Pauli distinguishes between gel possessing a structure and jellies "in which demonstrable structure need not be presupposed" the latter are, of course, the systems which we ar now considering. Pauli postulates as the necessar condition for gel formation electric neutrality of th particles "which then enter into the mutual relation characteristic of the solid state." Considering ou very incomplete knowledge of the solid state, thi view renders nugatory all attempts to demonstrat or elucidate gel structure by the investigation of *e.g.*, the elastic properties.

The assumption of heterogeneity and of a specia structure in gels is older than the opposite theory and has undergone various transformations with th development of the science and with the improve ments in the means of observation. Its chie support at present is the fact that emulsoid sols which set to gels, are generally recognised as hetero geneous and disperse systems, and there is n

reason to assume that these characteristics are lost in the transformation to gel. Wo. Ostwald maintains that the state of aggregation remains the same, *i.e.*, that gels (the fresh gels rich in dispersion medium are referred to) are systems of two liquid phases, although these liquids may be somewhat anomalous. Such systems would have to have a definite geometrical configuration, and this entails some difficulties in accounting for their elastic properties, which the author has attempted to analyze (*Trans. Faraday Soc.*, Vol. XII., Part 1, 1916). The view is supported, *inter alia*, by the continuity of the transformation as traced by viscosity measurements. The uncertainty of this criterion has already been pointed out (p. 82), and evidence of a discontinuity is provided by an interesting and little studied phenomenon, the shape of gas bubbles formed in the gel. Such bubbles, which can be produced by a variety of means, are always lenticular (E. Hatschek, *Koll.-Zeitschr.*, *15*, 226, 1914), while gas bubbles in a liquid at rest—however viscous—are, of course, spherical. It is possible to produce such bubbles during the transformation, and to note an abrupt change from the spherical to the lenticular shape, which, as stated, cannot be explained by a mere continuous increase in viscosity.

The earliest attempts to ascertain structure directly by microscopic examination are due to Bütschli (1892–1900), who investigated silicic acid and elastic gels with heroic magnifications. The influence of Quincke, who assumed a "foam cell" structure in many amorphous substances, manifests itself in these investigations. In cases, *e.g.*, gelatin, where the microscope did not reveal a structure, a "honeycomb" configuration showed itself after treatment with hardening agents such as chromic acid. In view of the permeability of gels, the walls of such a honeycomb, *i.e.*, polyhedral structure, must

either offer practically no resistance to the pass
of solutes, or must themselves be perforated. T
results must be received with caution on two distii
grounds: for one thing the interpretation of mic
scopic images of objects of this magnitude is diffici
as readers who may have examined such well-kno
test objects as Pleurosigma with very high pow
need not be reminded. For another, the structi
revealed after the use of hardening agents may no
as emphasized by Pauli—have been a pre-exist
one at all. Even if it is, it is not the ultim
structure, which from ultra-microscopic observati
is certainly sub- and more probably amicroscopic

The ultra-microscopic study of gel formati
combined with other evidence which has beco
available with the progress of the discipline, has
Zsigmondy and other investigators to adopt w
some modifications a theory originally propounc
on *à priori* grounds by Naegeli to account for
properties of elastic gels. The element of structu
according to him, is a molecular aggregate, genera
anisotropic, which he calls a " micella " (diminut
of *mica,* a crumb). These preserve their in
viduality in the sol and in the gel state; the lat
is caused by their aggregation or linking togeth
What geometrical form this linking takes is unc
tain, and of course the possibilities are v
numerous: a filamentous structure seems as proba
as any, and interesting ultra-microscopic obser
tions of filament formation have been described, *e*
by McBain. A system of strands or an open net
meshwork would account for the easy diffusion i
gels, and for the fact that liquid containing
colloid can be pressed out of them. This l
phenomenon has been studied and emphasized
Hardy; whether any conclusion regarding
distribution of the colloid in the two phases c
stituting the gel can be drawn from the respect

concentrations in the expressed liquid and in the residue must, however, be doubtful.

Von Weimarn, who obtained transparent gels of a number of substances by reactions between very concentrated solutions as well as by other processes, all of which in principle amount to producing suddenly a very high degree of supersaturation, looks on this type of gels as composed of ultra-microscopic crystals. Bradford has recently (*Bioch. Journ.*, *12*, 351, 1918) attempted to extend this view to gels like that of gelatin, which is not known in the crystallized state; the evidence adduced by him will require strengthening before it can be generally accepted.

In this connection it is of interest to mention the formation of very typical gels from a material which occurs in well-defined crystals. Several instances are known, of which the most striking is camphorylphenylthiosemicarbazide, which has been investigated by the author (*Koll.-Zeitschr.*, *11*, 158, 1912). The substance crystallizes in macroscopic needles, is slightly soluble in cold and readily in boiling organic solvents, *e.g.*, alcohol, carbon tetrachloride or toluene. If a 5 per cent. solution in boiling alcohol is allowed to cool *slowly*, the substance crystallizes in well-developed crystals. If the solution is cooled very rapidly, it sets to a clear gel with a slight bluish opalescence similar to that of silicic acid gel. On standing, crystal rosettes and similar aggregates begin to form and grow with a rapidity depending on the temperature, liquid is segregated, and the crystals finally sink to the bottom in clear, cold-saturated solution. If a 5 per cent. solution of the compound in boiling carbon tetrachloride is poured into a volume of warm liquid paraffin sufficient to make the final concentration about 1 in 350, the mixture on cooling sets to a gel as clear as glass, which persists for many months, although groups of small crystals may become visible.

In this instance it is impossible to escape the conclusion that gel formation is due to the segregation of ultra-microscopic crystals from a highly supersaturated solution; larger crystals then grow at the expense of smaller ones, since the substance is—though very slightly—soluble in the cold solvent. The rate of growth is naturally controlled by diffusion and therefore by the viscosity of the medium. This alone is, however, *not sufficient* to account for the formation of a coherent and elastic gel, for the following reason. If we assume the supersaturation to be equal to the total amount of substance present, we have about one part in 350, and it is easy to produce numerous compounds forming needle-shaped crystals—*e g.*, calcium sulphate, calcium carbonate as arragonite, etc.—in the same supersaturation without obtaining anything resembling a gel. Some form of linking or continuous structure still seems necessary to account for the characteristic properties of the gel.

The most probable view is, therefore, that in all cases of gel formation there is a linking of the elements of one phase into some continuous structure, probably largely developed in one dimension. Whether this consists of single filaments, of strands or fibrils of such, or of a more complicated network, or finally whether in some cases the structure consists of crystals twinned or otherwise interlinked, must be left open. The term "gel" is, as already pointed out, indefinite, and simply designates a body which, while containing a large amount of liquid, shows some of the properties of a solid, inasmuch as it maintains its shape and exhibits elasticity. The range of applicability of the term has, indeed, been the subject of controversy in specific cases, such as soap. It seems advisable to use it exclusively for systems which do not show elements of structure of microscopic size, though possibly this distinction is also arbitrary.

CHAPTER XXI.

We have already had occasion to emphasize the importance of the large boundary surface between the phases of a disperse system, inasmuch as it influences the electrical properties, and, in the case of two liquid phases, has an obvious bearing on the viscosity. We have now to consider a very large and very varied class of phenomena in which this surface is the determining factor, all of which may be comprehensively described as changes of concentration in one phase at its boundary surface with another phase. A study of these changes will enable us to form theoretical views of some fundamental properties of colloidal systems of which, so far, only a description has been given.

Many instances of such surface phenomena will be familiar to the reader, either from text books or from actual experience. One is, for instance, the capacity of charcoal to condense large volumes of gases, of which advantage is taken for obtaining extremely high vacua and for removing poison gases from the atmosphere. A related property of charcoal, that of taking out of solutions colouring matter or the higher alcohols constituting "Fusel oil," has been known since the end of the eighteenth century and is used industrially on a large scale; china clay and fuller's earth are also employed for purposes of the same kind. Another phenomenon of the same description is the power possessed by gels like gelatin or isinglass of taking down turbidities in organic extracts. An instance familiar to the analyst is the well-known fact that the concentration of many

solutions, *e.g.*, of lead salts, is perceptibly reduced by filtration through paper—that is, by contact with a large number of cellulose fibres.

This list could be extended very largely, but the instances given are sufficient to show that in all cases the effect is produced at a boundary surface of very considerable extent. What occurs is that certain substances present in solution are concentrated and somehow held at these surfaces, and this change in concentration is now generally called adsorption.

The occurrence of these changes also provides us with the clue to their investigation. We have already, when discussing emulsions, referred to the fact that the surface of a liquid against air (more strictly, against its own vapour) or against a second liquid is in tension, known as *surface tension* in the former and as *interfacial tension* in the latter case. This tension is an extremely well-defined physical constant, and can be measured by a number of methods. For details of these the reader must be referred to the text books of physics or physical chemistry; they all depend on the tendency of the tension to reduce the surface to a minimum in equilibrium with the other forces—*e.g.*, gravity—acting on the body of liquid under examination. A practical acquaintance with such measurements, even when slight, will lead rapidly to the discovery that surface tension is very easily affected by exiguous amounts of contaminations, such as water may take up from the air in a few minutes.

As it takes work to produce or enlarge a liquid surface, it is the seat of energy which is measured by the product of surface into surface tension per unit length and which, of course, tends to become a minimum. We already know one way in which this may be accomplished, *viz.*, by the surface becoming a minimum surface; thus a drop of liquid falling

freely in a vacuum or suspended in another liquid of the same density assumes spherical shape, the sphere having the minimum surface for a given volume. Obviously this is only possible where both phases are easily deformable, *i.e.*, when both are liquid, or one liquid and the other gas.

The question now arises whether such tensions and energies also exist at the surfaces gas-solid and liquid-solid, especially in view of the instances quoted above, all of which refer to such systems. It is obvious that the immediate methods of demonstrating and measuring such tensions, as applied to easily deformed phases, fail, since the surface of the solid is not easily altered and does not adjust itself to the tension. We can, therefore, only conclude by various inferences, which cannot be detailed here, that such tensions do actually exist, and the evidence on this point is quite conclusive. The question then arises whether the surface energy at the boundary of a solid can be varied and reduced to a minimum by some other means. Since it is a product of two factors, it can of course be reduced by reducing either ; in the case of a solid the surface is constant and any reduction which may occur must be due to a reduction in the surface tension. It is at least a reasonable assumption that *a change in concentration at the boundary surface may be accompanied by such a reduction.* If this assumption is correct, such a change ought to take place, and this is what actually happens.

We have thus come to the conclusion that, if in a two-phase system a change in the concentration of the liquid or gaseous phase will lead to a decrease of surface energy, this change will take place : to prove this view we have to investigate whether in all cases where such changes appear there is a diminution of surface tension. A change of concentration can occur in the gas phase if it is compressed at the boundary surface, or in a solution if the solute is

accumulated at the boundary. Now we know that charcoal, for instance, both condenses gases on its surface and removes colouring matter from solution, but, as already pointed out, we have no means of measuring the surface tension. We must accordingly obtain evidence by studying similar phenomena under conditions which permit such measurements, and this is possible by investigating the behaviour of a mercury surface against gases. The subjoined table gives the surface tension σ of mercury against vacuum (strictly against mercury vapour only) and various gases, one value being taken immediately after formation of the surface, the other one hour later :—

Mercury exposed to :	σ fresh surface.	σ after one hour.
Vacuum (15°)	436	436
Hydrogen (21°)	470	434
Oxygen (25°)	478	432
Nitrogen (16°)	489	438
Carbon dioxide (19°) ..	480	436
Dry air (17°)	476	429
Moist air (17°)	481	429

It will be seen that the two values measured *in vacuo* are the same, that is, no change has taken place after one hour. In all the gases, however, the final value of the surface tension is considerably lower than the initial one, and this change is accompanied by the condensation of gas on the mercury surface. The rate of change is characteristic for each gas, and curves plotted with the times and tensions as co-ordinates agree very well with the corresponding time-pressure curves obtained with solid adsorbent materials exposed to the same gases. As the decrease in the surface tension mercury-gas is accompanied by compression of the latter, we must at once conclude that the surface tension of

mercury should be lowered by rising gas pressure—a conclusion which has been experimentally verified.

The case discussed furnishes us with an instance in which the concentration—or, in other words, the pressure—of gas has been altered at the surface of a liquid with a reduction of surface energy, and we conclude that the same conditions hold good at the boundary solid-gas. We may now consider an instance at the boundary liquid-gas in which the change of concentration occurs in the *liquid* instead of the gas phase, with the object of once more verifying that it is accompanied by a reduction of the surface tension. We are already familiar with one simple criterion of lowered surface tension: froth formation. If we therefore take a solution exhibiting this characteristic and produce the largest possible surface by making a froth, the latter ought to contain the dissolved substance in greater concentration than the liquid in bulk. This reasoning has also been verified experimentally by several observers, especially by Miss Benson, for mixtures of water and amyl alcohol, which froth copiously. Air is drawn through the mixture and carries the froth formed over into a second vessel: this froth and the bulk are then analyzed separately. An excess of about 5·5 per cent. of alcohol is found in the froth, which result confirms our reasoning.

The experiment just quoted refers again only to the surface liquid-gas, but it can be shown, *e.g.*, with albumin sols, that this surface and the interface liquid-liquid behave alike. Such sols froth copiously, and it was shown by Ramsden that by vigorous shaking of dilute sols practically the whole of the albumin went into the froth, incidentally becoming insoluble. The same thing occurs at the interface liquid-liquid; if an albumin sol is shaken vigorously with an organic liquid, *e.g.*, chloroform or carbon tetrachloride, the latter is broken up into small drops

which do not coalesce even after long standing owing to the formation of an albumin membrane If the excess of sol is poured off and replaced b water the drops still fail to coalesce, the membran being insoluble just like the albumin concentrated i froth, *i.e.*, at the surface air-liquid.

We have thus some evidence to support the vie that the changes of concentration, classed togethe as adsorption, on a surface are due to the tendenc of surface energy to assume a minimum value, an that they occur if an *increased concentration leads t a reduction of the surface tension.* Our whole know ledge of the matter, however, is not exclusively base on such reasoning, which, as far as the solid surfac is concerned, rests on the uncertain ground of analog but the principal proposition has been proved b thermodynamical methods by Willard Gibbs. H arrived at the following expression :—

$$U = -\frac{C}{RT}\frac{d\sigma}{dC},$$

in which the symbols mean :

U excess of substance in surface layer.
C concentration in bulk of liquid,
σ surface tension,
R the gas constant,
T the absolute temperature.

The formula contains the differential coefficient c the function connecting surface tension with cor centration, which is, of course, positive if bot change in the same sense, and negative if they chang in opposite senses. This, in conjunction with th minus sign on the right hand of the equation, show at once that there will be a negative excess, *i.e.*, *reduced* concentration in the surface, if the surfac tension *increases* with increasing concentration, an a positive excess, *i.e.*, *increased* concentration in th surface, if the surface tension *decreases* with increas

ing concentration. The latter is the more frequent case and agrees with the instances previously given; the former has also been observed experimentally, and is known as *negative adsorption.*

Various attempts to test the formula quantitatively have been made; for a description of these and a full discussion of the difficulties involved the reader is referred to "Surface Tension and Surface Energy." One fundamental difficulty must, however, be pointed out here. The coefficient $d\sigma/dC$ can, of course, be determined only from measurements of σ at different concentrations, and these are possible only at the interface liquid-gas or liquid-vapour. The assumption that $d\sigma/dC$ will be the same at the interface solid-liquid, if a solid adsorbent is in question, is not susceptible of proof. As a matter of fact, anomalous cases are known, in which the solute *raises* the surface tension ($d\sigma/dC$ is positive), and is yet adsorbed on a solid adsorbent. Instances are sugar on charcoal (G. Wiegner, *Koll.-Zeitschr.*, *8*, 126, 1911) and sodium chloride on colloidal sulphur (Sven Oden, *loc. cit.*, p. 42).

CHAPTER XXII.

FURTHER conclusions can be drawn from the Gibbs formula. As the absolute temperature appears in the denominator, the excess in the surface or, in other words, the amount adsorbed, varies inversely with the temperature and decreases as the latter rises. This relation holds generally, though only qualitatively. It can also be shown that a *small* amount of dissolved substance can *lower the surface tension greatly*, but can only *increase it slightly*.

This statement, though perhaps unexpected at first sight, becomes intelligible when we remember that surface tension manifests itself only in the surface layer and depends purely on the composition of the latter. If a dissolved substance increases the surface tension, the formula tells us that its concentration in the surface layer is less than in the bulk of the liquid, and its effect thus tends to counteract itself. On the other hand, if it reduces the surface tension, it accumulates in the surface layer, thus enhancing its effect. As a matter of experience, minute amounts of accidental contaminations often reduce the observed values of surface tension considerably; while increases caused by such unintentional admixtures are not met with.

When more than one solute is present the process necessarily becomes complicated, but one or two points may be discussed briefly. It is, generally speaking, probable that the various substances may not be adsorbed to the same extent, in which case one or the other may be removed selectively, *e.g.*, colouring matter from organic extracts. Where a

compound is dissolved in a dissociating solvent the ions may likewise not be adsorbed equally, and the solution, originally neutral, may be acid or alkaline after adsorption; this has also been observed experimentally, *e.g.*, by van Bemmelen in the adsorption of potassium sulphate by gels, when the remaining solution was found acid, the K ion being adsorbed to a greater extent than the SO_4 ion.

If an adsorbent is placed successively into two different solutions the case can occur that the second solute is adsorbed more strongly than the first, which it will then displace more or less completely. Thus, if charcoal is shaken with a dilute solution of Fuchsin, the dye is adsorbed and the liquid after filtering or centrifuging off the charcoal is colourless. If the charcoal is now placed in a dilute solution of saponin the latter—which lowers surface tension greatly and accordingly causes frothing in exiguous concentration—is strongly adsorbed and displaces the dye, so that the solution turns red.

It is obvious that the amount adsorbed, other things being equal, is proportional to the active surface. All substances employed as adsorbents have a very large surface per unit mass; it is unfortunately impossible to measure it, and comparison between two adsorbents leaves open the question whether differences in their power of adsorption are due to differences in specific surface, or to specific differences in the materials, or, of course, to both. Apart from the materials like charcoal, fullers' earth, etc., which are familiar, one which has recently acquired some prominence deserves mention. This is the modification of aluminium hydroxide, called by Wislicenus, who first used it for the quantitative adsorption of tannin, "*gewachsene Tonerde*," *i.e.*, "sprouted alumina." It is obtained by allowing aluminium slightly contaminated with mercury to oxidize in a moist

atmosphere; the microscopic structure singularly resembles that of a unicellular fibre, while the ultimate structure is probably that of a gel. That the adsorbent effect is due to the latter structure is shown by its remaining unaltered when the substance is dehydrated at red heat.

While we have thus a number of qualitative data regarding the phenomenon, important questions are still open: whether it proceeds to any definite end point or equilibrium, what time is required to reach such equilibrium, if it does exist, and whether the equilibrium concentrations can be formulated mathematically.

As regards the first point, this is settled, inasmuch as a definite equilibrium can be shown to exist in cases of pure adsorption, *i.e.*, when chemical action and other complications, some of which are still obscure, are excluded. One of the first experiments dealing with this aspect of the problem was made by Wilhelm Ostwald, who placed a quantity of charcoal in dilute hydrochloric acid, and after a certain time determined the concentration of the latter. If, then, a portion of either the charcoal or of the acid was removed no further change took place, which tends to show that the two concentrations, in the surface layer and in the bulk respectively, are independent of the masses, a necessary condition for an equilibrium. Further decisive experiments were carried out by Freundlich, who placed charcoal in solutions of acetic and of benzoic acid of known strengths and determined the amounts adsorbed. The same quantities of charcoal were then placed into half the volumes of acid of double the concentration used in the first experiments, and after a time an equal volume of solvent was added, bringing the total volumes to those used in the first instance. If there is a definite equilibrium between the adsorbed quantities and the concentrations in the bulk of the

solution, the final concentrations in the second set of experiments must be the same as in the first, and Freundlich in fact found this to be the case.

As regards the time required for reaching an equilibrium, it must be remembered that the solute can reach the adsorbing surface only by diffusion, which therefore controls the time, provided the liquid and adsorbent are at rest. Adsorption experiments are therefore always carried out with agitation, generally under specified uniform conditions. Equilibrium is then as a rule reached very rapidly, but numerous cases are recorded in which it is not final, and further slow withdrawal of solute extends over a considerable period. A striking instance is the adsorption of iodine by charcoal (J. W. McBain, *Trans. Far. Soc.*, *14*, Pt. 3, 1919), which continues slowly for many months. There is at present no definite explanation of this and similar anomalies; in some instances chemical action, although at first sight highly improbable, has been demonstrated, *e.g.*, in the adsorption of permanganate and of oxalic acid by charcoal. In this connection it is worth emphasizing that charcoal, which has been used more largely than any other substance in the study of adsorption, is extremely ill defined chemically and, whatever else it may be, is certainly not simply "carbon," although it is frequently so described in records of adsorption experiments.

The relation between adsorbed amount and equilibrium concentration was first deduced by Freundlich, who has also carried out a large amount of varied experimental work to test it. If we call the quantity adsorbed y, the quantity of adsorbent m, and the end or equilibrium concentration in the liquid (*after adsorption*) C, this relation takes the following form:—

$$\frac{y}{m} = aC^{\frac{1}{n}},$$

in which a and n are constants depending on nature of the solutions and the adsorbent. curve corresponding to the above equation was cal by Freundlich the "adsorption isotherm," but now more generally described as the concentrat function. It is a generalized parabola, and for n = it becomes the ordinary conic parabola.

It may be pointed out here that the formula is s very frequently, but quite incorrectly, spoken of an "exponential" one. An exponential express is one containing one of the *variables*—in the pres case these are y and C—as exponent, whereas exponent of the concentration function is a *consta* It is an interesting fact that this constant va within comparatively narrow limits for the m widely different solutes, viz., roughly speaki between $n = 2$ and $n = 10$.

The principal deduction from the equation obvious: the amount adsorbed, other things be equal, increases much more slowly than the conc tration or, in other words, is proportionately great in dilute solution.

The concentration function has been tested, a the exponents $1/n$ determined, for many solutes a solvents. The table below is due to Freundlich

Adsorbent.	Solvent.	Solute.	$\frac{1}{n}$.
Blood charcoal ..	Water	Formic acid ..	0·45
,, ,, ..	,,	Acetic acid ..	0·42
,, ,, ..	,,	Benzoic acid ..	0·33
,, ,, ..	,,	Picric acid ..	0·24
,, ,, ..	,,	Chlorine	0·29
,, ,, ..	,,	Bromine	0·34
,, ,, ..	Benzene	Benzoic acid ..	0·41
,, ,, ..	,,	Picric acid ..	0·30
,, ,, ..	Water	Patent Blue ..	0·19
Wool	,,	Patent Blue ..	0·15
Silk	,,	Patent Blue ..	0·16

The table gives a good idea of the limits between which the exponent varies, and a further point of interest is raised by the behaviour of the same solute —patent blue in water—towards three adsorbents as different as charcoal, wool and silk. The value of the exponent does not differ greatly in the three cases, and it has been observed with many solutes that the influence of the adsorbent is slight compared with that of other factors. It must, however, be remembered that the comparison between various adsorbents is based on *equal weights in equal volumes of solution*, while the important factor is the surface, which we have no means of determining and comparing, at least with any approach to accuracy. Specific effects are, of course, possible; thus Michaelis and Rona (*Koll.-Zeitschr.*, *25*, 225, 1919) conclude from experiments with solutions of acetone and some higher alcohols, with various adsorbents, that the action of charcoal is specific and not explicable merely by any probable difference in active surface compared with the other materials investigated.

It is fairly well established that the *order* in which various solutes are adsorbed is the same for different adsorbents; if a substance A is more strongly adsorbed than another B, and the latter more than C, by charcoal, the same order will hold good for other adsorbing materials, although the numerical ratios may differ.

Another question of importance has not been touched on so far—that is, the effect of the solvent in cases where a substance is soluble in more than one liquid. It is well known, even from general experience, that the same substance is not adsorbed equally out of solutions in different solvents, and that adsorption is much slighter in organic solvents than in aqueous solution. Thus Freundlich gives the following figures for the

adsorption of benzoic acid out of solutions of equal strength in :—

Water	..	..	4·27
Benzene	..	..	0·55
Ether	..	..	0·30
Acetone	..	..	0·30

The difference is probably explained by the high

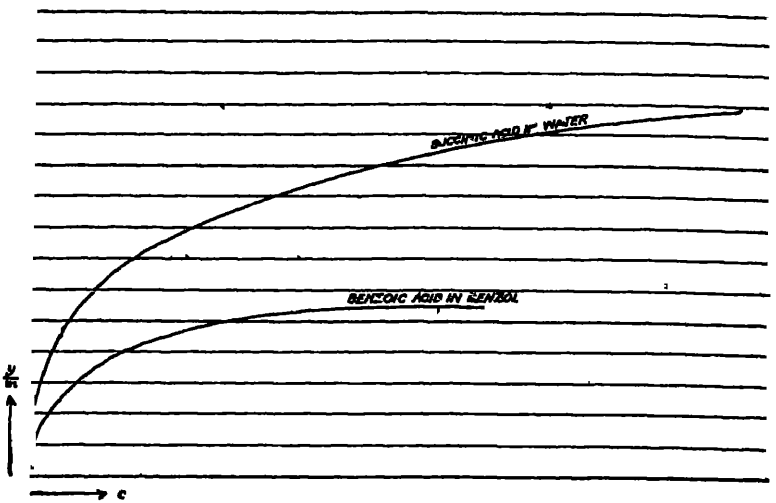


FIG. 18.—TYPICAL ADSORPTION CURVES.

surface tension of water (73 dynes/cm.) compared with that of organic liquids, *e.g.*, benzene 28·8, acetone 23 and ether 16·5 dynes/cm. The lowering of surface tension caused by solutes is correspondingly greater in water, and therefore also the adsorption from aqueous solutions. This difference is used practically for removing or recovering from an adsorbent substance taken up by it out of an aqueous solution. If, for instance, a dilute solution of a dye,

like crystal violet, is shaken with sufficient charcoal, the dye may be removed completely by the latter. If the water is now replaced by alcohol, the adsorption from which is much lower, the surface concentration of the dye on the charcoal is in excess of that which would establish equilibrium and a great portion of it goes into solution in the alcohol. It is hardly necessary to point out that this effect is quite distinct from the displacement by another solute described on p. 139.

Two typical adsorption curves are shown in Fig. 18. They are due to Freundlich and strikingly illustrate the parabolic shape characteristic of the normal, uncomplicated phenomenon. Similar curves which can be represented fairly accurately by equations of the form given on p. 141 have been obtained by Freundlich and other investigators for numerous other non-electrolytes. It must, however, be mentioned that a number of cases are known in which the concentration function appears to be of a fundamentally different type, and more particularly some in which adsorption *reaches a maximum at definite concentrations and decreases with a further increase in concentration.* An interesting instance is afforded by the adsorption of Night Blue on various adsorbents, studied by Biltz and Steiner (*Koll.-Zeitschr.*, *7*, 113, 1910). Fig. 19 shows the curves obtained with cotton as adsorbent, (1) being that for the technical dye at

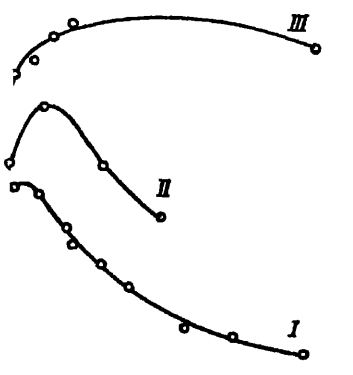


FIG. 19.—ANOMALOUS ADSORPTION OF NIGHT BLUE BY COTTON.

room temperature; (2) dialysed dye at room temperature; and (3) dialysed dye at boiling point. The curves agree in type and show a well-marked maximum. As Night Blue is a positively charged colloid, while cotton in the solutions used is probably negative, adsorption may be complicated by electrical factors, though these do not very readily account for the maximum.

Such complications are even more marked in the case of strong electrolytes, and at present very little that is definite can be stated regarding their adsorption. In many instances, *e.g.*, alkaline nitrates and sulphates, adsorption is extremely slight; that of the chlorides is negative according to Lagergren, while Sven Oden, by various inferences, reaches the conclusion that sodium chloride is adsorbed *positively*, and to a considerable extent, by colloidal sulphur (*loc. cit.*, p. 42). Salts of heavy and noble metals (lead, gold) can be removed almost completely from dilute solutions by charcoal, but the liquid is left strongly acid. Various explanations are possible: from gold salt solutions the hydroxide formed by hydrolytic dissociation may be adsorbed, leaving the free acid in the solution. Although the first step in these processes may be a pure adsorption, the final condition is not a reversible equilibrium. The extreme complications which may arise are well illustrated in a series of experiments by Oryng (*Koll.-Zeitschr.*, *11*, 169, 1912) on the adsorption of potassium permanganate by charcoal. An apparent equilibrium is reached rapidly, and the solution is then strongly alkaline, *i.e.*, $K^{\cdot}$ is not adsorbed in equivalent amount with MnO_4'. On further standing or shaking, however, both MnO_4' and $K^{\cdot}$ continue to be withdrawn from the solution. Experiments were made to explain this secondary phenomenon and seemed to indicate a chemical reaction between MnO_4' and the charcoal, oxalic acid and MnO_2 being

formed. The continued disappearance of $K^{\cdot}$ is most probably due to adsorption by the MnO_2 thus formed.

It has been necessary to point out thus briefly the unsatisfactory state of our knowledge regarding adsorption from electrolyte solutions because the latter are of particular importance to the colloidal chemist, and because, as we shall see later on, conclusions drawn from the uncomplicated concentration function have been put forward to explain phenomena observed in solutions of electrolytes.

CHAPTER XXIII.

THE different degree of adsorption of *two or more* substances present in a solution can be strikingly demonstrated, and can be utilized for proving their presence in extremely minute quantities, by allowing the solution to rise by capillarity in some porous adsorbent material, *e.g.*, in strips of white filter paper. While this takes place the dissolved substances are adsorbed by the fibre, so that beyond a certain height the liquid in the paper consists of pure solvent only. Different solutes, generally speaking, rise to different heights and can be identified by their colour or, if colourless, by appropriate reactions. The process can be demonstrated, for instance, with a dilute solution of turmeric and picric acid, which is allowed to rise in a strip of white filter paper about 12 ins. long. The paper is stained a uniform pale yellow, but if it is then exposed to ammonia only the lower portion turns brown, showing that the turmeric pigment has not risen as far as the picric acid. The method, which deserves to be more widely known than appears to be the case, may be used for showing the presence of colouring matter or preservatives in articles of consumption, and for many similar purposes even when very small quantities only are available. It has been developed—under the title of " capillary analysis "—principally by F. Goppelsroeder, who has demonstrated its extreme sensitiveness in favourable cases.

A promising modification of the method has recently been suggested by W. Kraus (*Koll.-Zeitschr.*, *28*, 161, 1921), which is based on the observation that

when a porous body impregnated with a solution is allowed to dry, the solutes are concentrated near the surface. Strips of filter paper, saturated with the solution to be examined, are placed between glass plates, one end being allowed to protrude and to dry. The solutes wander towards the drying end and separation takes place, those most strongly adsorbed being left behind, while the constituents which are adsorbed slightly are concentrated in or near the exposed end of the strip.

It is obvious that in all instances in which reactions take place in the presence, or lead to formation, of finely divided solid matter, adsorption is possible, and may account for changes in concentration and losses. It offers thus a somewhat easy explanation of many such phenomena, which, however, should not be taken as established without investigation. In the first instance it is necessary to demonstrate that a real reversible equilibrium has been attained, since the adsorption equation holds only for that state. Measurements at different concentrations must then be made, and if the results plotted in the usual manner lead to curves of the parabolic type shown in Fig. 18, the evidence of adsorption may be considered strong, though not absolutely conclusive, as the parabolic type of curve is not uncommon. If the results show a marked divergence from the type, further investigation is certainly called for. Adsorption, if it takes place at all, may then be accompanied or followed by some other process, such as chemical combination or penetration into the interior of the adsorbent.

A process which, in many ways, may be looked upon as the converse of adsorption, is the extraction of a substance containing an admixture with a solvent in which the latter only is soluble. It is evident that if there is simple mechanical mixture, and if a sufficient quantity of solvent is employed, the whole

of the soluble matter will be extracted by this first lot of solvent. It is equally obvious that this cannot happen if the second substance is *adsorbed* by the first; in that event the first lot of solvent will, indeed, remove a large fraction of the soluble matter, but as much of it as establishes equilibrium under the given conditions will be retained. A second lot will again remove a—much smaller—quantity, and so on. If a curve is plotted with the—preferably equal—volumes of solvent as abscissæ, and the amounts of soluble matter still retained by the insoluble phase as ordinates, curves of a hyperbolic type are obtained, and it is quite easy to construct from these the inverse, *i.e.*, concentration-adsorption function, as will be clear from an actual example. Rubber, as is well known, contains varying amounts of "resin," *i.e.*, of substances soluble in acetone, and the results of extraction with equal successive amounts of that solvent are shown in Fig. 20, taken from an investigation by D. Spence and J. H. Scott, published in the *Kolloid-Zeitschrift*. The amounts of resin still retained after each extraction are plotted as ordinates in full line at equal distances apart. It will be noticed at once that the first lot of solvent extracts a very large proportion of the total resin content, as shown by the length *ab* on the ordinate *ac*. Similarly, the portion extracted by the second lot of solvent is given by the—much smaller—length *a'b'* on *a'c'*. The curve resembles an hyperbola, and it can easily be shown graphically that the whole process is an inverted adsorption. If we consider the two portions of the ordinate *ac*, we see that *ab* has gone into solution, while *bc* is retained by the rubber. The latter, therefore, represents the amount adsorbed, which is in equilibrium with the concentration produced by dissolving the quantity *ab*. If, accordingly, we plot the lengths *ab*, *a'b'* as abscissæ, and the lengths *bc*, *b'c'*, as ordinates, we obtain a

curve which must have the character of the adsorption curve if the extracted matter was really adsorbed on the insoluble portion. The curve is plotted in dotted line, and is of the familiar parabolic type.

(In the actual plotting of the dotted curve the

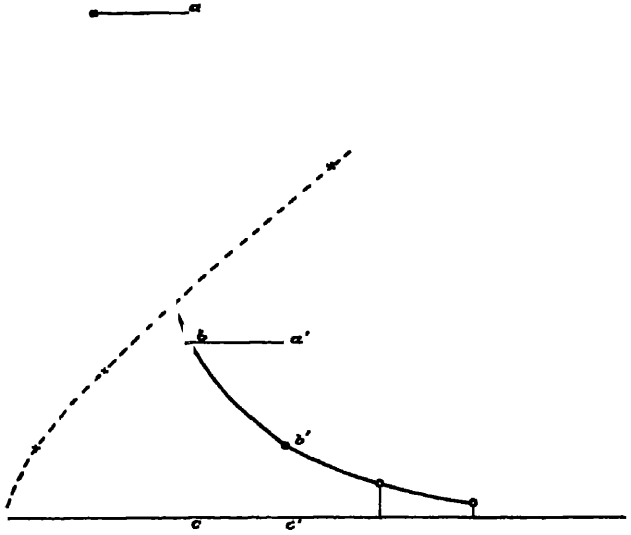


FIG. 20.—EXTRACTION OF ADSORBED SUBSTANCE.

ordinates have been doubled to obtain a larger scale.)

We have so far considered only phenomena in which the change in surface energy has been held to be the determining factor, and have disregarded the fact, with which we are already familiar, that boundary surfaces are generally the seats of electric

charges. It is more than probable that these m affect adsorption, and there are some striki phenomena in which the electric factors play t most important or, indeed, an exclusive part. If, instance, a dialysed sol of ferric hydroxide is pass through a column of carefully purified and ignit quartz sand, the ferric hydroxide is complete retained and only clear water leaves the end of t column for a time. The same thing occurs with sol of Night Blue, as has been shown by Dreaper a Davis. In both cases the sand is capable of retaini only a definite quantity of disperse phase, so th the process is obviously not a filtration. Both fer hydroxide and Night Blue belong to the not ve numerous class of positive colloids, while sili assumes a negative charge in contact with wate It is therefore reasonable to assume that the positi colloidal particles are discharged and retained t the negatively charged sand grains. This view borne out by the fact that acid sols of ferric hydroxid in which the H ion concentration is sufficient neutralize or reverse the charge on the sand, pa through practically unchanged. Night Blue retained with such tenacity even by smooth gla surfaces that vessels which have contained the s cannot be washed clean with water alone.

The vast general importance of adsorption hardl needs to be emphasized. Its close connection wit and special importance in, the study of colloids also obvious; since all the systems dealt with unde this head possess very large interfaces, adsorptio is an essential, if sometimes very obscure, factor the whole complex of phenomena to be observe Thus adsorption undoubtedly takes place, not onl in gels, but also on the surface of the disperse phas in sols. This has been proved directly, by means conductivity measurements, by Wolfgang Ostwal and by several other observers. Many authoritie

even hold that the electric charge on the particles is due to absorbed ions, and that its neutralization or reversal, with coagulation, by electrolytes belongs to the same category. This aspect of the subject will receive detailed consideration in the next chapter.

CHAPTER XXIV.

We are now in a position to survey very b the theories which have so far been advance account for the electric charges in disperse syst which we have found throughout to be a fact fundamental importance. At the outset it ma useful to remind the reader that, while theory is highly controversial, the *facts* are securely establi for a large number of systems and can easil ascertained for any fresh case by recognized met such as cataphoresis, etc.

The formal mathematical treatment of phenor like electric osmosis and cataphoresis rests on assumption that at the boundary surface of the phases there exists an electrical *double layer*, a cept and term introduced by Helmholtz. This m two layers or surfaces of opposite sign and a def difference of potential separated by a small dista The mathematical treatment further implies the *whole of the double layer lies in the liquid phase*, the one charge in the layer of liquid immedi adjacent to the solid phase, and the opposite ch at a small distance away from the interface. I electric field the two faces of the double layer displaced towards each other with the result whichever phase is free to move travels towards pole carrying the opposite sign.

This treatment has been developed by Helmh Lamb and v. Smoluchowski, and leads to quantita results, but makes no assumptions about the o of the double layer itself. *A fortiori* it does explain the conditions which we have descri

such as the large number of suspensoids in which the disperse particles are negatively charged, the positive charge in a fairly limited class like the hydroxide sols, and the reversal of the charge by appropriate ions. An empirical suggestion to account for the *sign* of the charge has been put forward by Coehn, according to which, of two phases in contact, the one with the higher dielectric constant assumes a positive charge. The dielectric constant of water is exceptionally high (water 81, ethyl alcohol 26, benzene 2·3, etc.), so that the majority of substances should be negatively charged in contact with it. But apart from not in any way explaining the origin of the charge the rule fails to account even for the sign in such cases as the hydroxides. Nothing appears to be known regarding their dielectric constants, but in the absence of such knowledge it is difficult to believe that stannic acid, which is negative, should have a lower, and ferric or aluminium hydroxide, which are positive, a higher dielectric constant than water.

A further difficulty is the fact—of great importance in other respects, although frequently overlooked—that the same substance may have *either a negative or a positive charge*, according to the method by which it is produced as disperse phase. Lottermoser's method of preparing sols of the silver haloids has already been mentioned briefly (p. 43). According to the order of procedure these sols may be negative or positive: if the halogen ion is in excess throughout, the particles of silver haloid are negatively charged, while the opposite result is obtained by keeping the silver ion in excess throughout. Other cases of the kind are known: thus, although all the gold sols described in the literature are negatively charged, Morris-Airey and Long have prepared a positive sol, and Powis has described a negative ferric hydroxide sol. The instances given, although not numerous, are at any rate sufficient to show that sign of the

charge is not a specific characteristic of a given substance.

In view of this conclusion it is natural to look for the cause of the charge in the aqueous phase, or more precisely in the ions present in it. As has already been pointed out several times, the aqueous phase in all ordinary sols contains electrolytes, which are quite obviously connected with the formation and stability of the sols. One theory of the electric charge—put forward by various investigators, and elaborated by Freundlich—accordingly ascribes it to the *adsorption of ions* on the particles of disperse phase. Among the ions known to be easily adsorbed OH' and $H^{\cdot}$ are pre-eminent. Thus, to take one or two concrete examples, the reduction of gold is very generally carried out in alkaline solution; it has, indeed, been suggested (Pauli) that stable gold sols cannot be obtained except in alkaline media. OH' is accordingly present and, being an anion, imparts the negative charge to the particles. On the other hand, in the usual methods of preparing ferric hydroxide sol the medium is acid, *i.e.*, contains $H^{\cdot}$, which is adsorbed and imparts the positive charge to the disperse phase. If, however, ferric hydroxide is made by Powis's method—adding ferric chloric to an excess of caustic alkali—OH' is present and, being adsorbed, leads to the production of a *negative* sol.

The adsorbed ions must necessarily be assumed to be concentrated in the layer of liquid immediately adhering to the surface of the disperse phase, and to be surrounded by a layer containing an equivalent amount of ions of the opposite sign. We therefore have a double layer which, as postulated by the Helmholtz theory, lies entirely in the liquid.

According to Freundlich, the neutralization of the charge is also produced by adsorption, viz., of the ion with a sign opposite to that which gives the

particle its charge. The most immediately striking feature of electrolyte coagulation, the effect of valency, he explains by the following considerations:—

To neutralize a given charge, equivalent amounts of ions of different valency will have to be adsorbed, viz., the same effect will be produced by one univalent ion, 1/2 bivalent and 1/3 trivalent ion, or the ratio of the amounts to be adsorbed will be 6 : 3 : 2. Assuming the ions to be adsorbed equally, the same concentration function will represent them, so that the concentrations corresponding to these adsorbed amounts will be the abscissæ, the ordinates of which are in the above ratio. As we have seen (p. 142), the adsorbed amounts increase much more slowly than the equilibrium concentrations: if we assume the exponent in the adsorption equation to have the value 1/3, the end concentrations giving adsorbed amounts in the above ratio would be 216 (univalent) : 27 (bivalent) : 8 (trivalent).

How far the simple adsorption equation applies to the adsorption of ions is a difficult question, into which it is not necessary to enter. The assumption that different ions are adsorbed about equally is, in any event, untenable, as is evident even from the small selection of data given on p. 56. Quite recently Wolfgang Ostwald (*Koll.-Zeitschr., 26*, 28, 69, 1920), has reviewed a very large mass of data on electrolyte coagulation, and has come to the conclusion that Freundlich's theory—while selected sets of values can be found to conform to it—in a large number of cases fails to account for the effects of even closely related electrolytes.

These criticisms, of course, do not affect the theory which ascribes the original charge to adsorbed ions. Whether disperse particles would be electrically charged in a medium not containing ions, or whether stable systems of colloidal dispersity are possible,

in which the disperse phase is not charged, are questions of great importance in this connection, to which no answer is possible until non-aqueous systems have been studied more exhaustively than has been the case so far.

We must now consider briefly an important class in which the charge on the disperse phase need not be ascribed to adsorption: the soaps (p. 101) and the proteins (p. 89) are its most important representatives. The behaviour of the former is the simpler, and has been completely elucidated by the investigations of McBain and his school (for a very lucid summary see III. British Association Report on Colloid Chemistry, 1920). According to McBain, a soap, *e.g.*, sodium palmitate, dissociates into a number of sodium ions, and into a complex or "ionic micelle" of the following constitution:—

$$(NaP)x \,.\, (P')n \,.\, (H_2O)m,$$

i.e., a hydrated aggregate of undissociated palmitate molecules and palmitate ions, the number of the latter being, of course, equal to the number of sodium ions. The whole aggregate behaves as an anion, and the degree of hydration varies continuously with concentration and temperature. Its size is such as to bring it within the colloidal range of dispersity.

The proteins have been investigated by similar methods by Pauli and his pupils, and the results obtained are analogous. As we have seen (p. 90), the proteins form salts with either acids or bases; the former dissociate into a protein cation, and one or more ordinary anions, while the latter give rise to a protein anion and one or more ordinary cations. The protein ion, whichever its charge, is complex, hydrated and colloidal.

While the evidence that soaps and protein salts behave in this manner, viz., as "colloidal electro-

lytes," is fairly conclusive, the attempt made by Pauli to extend the theory of complex formation to *all colloidal systems* is likely to cause controversy. The attempt is based on careful electrometric determinations of the ion concentration in various hydroxide sols, of which two only shall be mentioned here. Ferric hydroxide, made from the chloride, is supposed to be a complex salt of the formula :—

$$x\mathrm{Fe(OH)_3} \,.\, y\mathrm{FeCl_3}$$

which dissociates into the complex cation: $x\mathrm{Fe(OH)_3} \,.\, y\mathrm{Fe}^{\cdots}$ and $3y\mathrm{Cl}'$. An analogous structure is suggested for stannic acid peptized by alkali :—

$$x(\mathrm{SnO_2}) \,.\, y\mathrm{SnO_3K_2},$$

which dissociates into the complex anion : $x(\mathrm{SnO_2}) \,.\, y\mathrm{SnO_3}''$ and $2y\mathrm{K}^{\cdot}$. Finally a complex structure has been ascribed even to colloidal gold (*General Discussion, Faraday Soc.*, October, 1920). In the alkaline reduction of gold chloride an intermediate step is the formation of an aurate, *e.g.*, $\mathrm{KO_2Au}$, and the particle is looked on as a complex of metallic gold and aurate, which latter dissociates into auric anion, giving the particle its negative charge, and a cation.

These views have only recently been put forward (although an earlier complex hypothesis has been formulated by Duclaux), and, while likely to cause controversy, are here mentioned briefly for the sake of completeness. Certain difficulties are obvious in the case of metal sols ; it is certainly possible to reduce $\mathrm{AuCl_3}$ or $\mathrm{HAuCl_4}$ without alkali, in acid solution, with ethyl alcohol at about 95° C., when the formation of an aurate appears improbable ; equally so is the existence of a silver compound with Ag in the *anion*, which would be necessary to explain the negative charge on the particles of all known silver sols.

The reader will realize, even from the very brief summary given, that our knowledge of the origin of the charge on colloidal particles is still very incomplete. It is, of course, quite possible that it may be produced by different causes in different systems, and that attempts to find a single explanation applicable to all cases are foredoomed to failure.

CHAPTER XXV.

IT now remains to devote a few words to applications of colloid physics and chemistry, both theoretical and practical. As regards the former, it has given the impetus to the study of the Brownian movement by Svedberg, Einstein, v. Smoluchowski and Perrin, which has afforded the most striking and convincing proof of the real existence of molecules. No such conspicuous success has yet attended the application of colloid science to the innumerable problems of physiology calling for elucidation, but this is a field full of the greatest promise. Swelling in water and in solutions of electrolytes, diffusion in gels and through membranes, the phenomenon of syneresis, the deposition of insoluble calcium salts or of silica in gel-like media, all have an important bearing on processes occurring constantly in living organisms. Encouraging starts have been made in many directions: to mention one or two examples only, the study of phase-reversal in emulsions (p. 76) has led to theories of protoplasmic structure and of the effect of "antagonistic ions" which, while in need of much further work, open a new way of approaching a difficult problem. The enhanced swelling in acid has been studied in its physiological aspect by Martin Fischer and his school, who emphasize its bearing on fundamental phenomena like muscle contraction and on morbid processes like œdema.

To take another branch of our subject, the study of adsorption is beginning to clear up a great number of debated questions in widely different fields

Van Bemmelen, the pioneer in this line of research, was led into it through studying the properties of soils, and its fundamental importance in this regard is now generally recognized (see General Discussion, Faraday Soc., May, 1921). At the other end of the scale, the synthetic preparation of the photohaloids, *i.e.*, coloured adsorption compounds of colloidal silver and a silver haloid, has solved an old and famous problem, the nature of the latent photographic image.

As regards practical or technical applications, the claims of colloidal chemistry are perhaps not quite as clear yet, and no useful purpose is served by exaggerating them. In this connection it may perhaps be well to remind the reader, not only of the youth of the whole discipline, but of the twofold way in which the development of a branch of science may bear on industries and arts. It may, of course, lead directly to new processes and manufactures: an instance is the production of squirted filaments of the refractory metals for incandescent lamps, which were made from the finely divided metal coagulated from its sol, before these metals could be drawn into wire. The much more general case—for which the growth of the chemical industries and of chemistry provides innumerable illustrations—is that it provides explanations of phenomena long known and dealt with empirically, and thus opens the way to further progress. In this direction colloidal chemistry finds itself in a position of particular difficulty, inasmuch as many of the industries dealing with typically colloid material, such as ceramics, the textile industries, the fermentation industries, tanning and some branches of dyeing, are as old as history, or older, and have attained a high degree of perfection partly empirically, partly, though much later, with the aid of chemistry. In all of them, however, there are numerous problems which have

so far withstood attempts at solution by the methods of pure chemistry. The number and importance of such problems will be vividly brought home to the reader of the three British Association Reports on Colloid Chemistry. For these questions a knowledge of the properties of colloids provides, if rarely an answer at the first approach, at least an entirely new method of attack. It is perhaps natural that in some cases this attack should take the—not very helpful—form of a mere restatement of the problem in the terms of colloid chemistry. But a good deal more than this has been accomplished and even published, and it is not surprising that industries of more recent origin should have shown a greater readiness to profit by new knowledge. Thus the difficulties arising in the manufacture of margarine have given a perceptible impetus to the study of emulsions, with results which, one may hope, have benefited the industry and are certainly an addition to our scientific knowledge. The increasing use of viscosity measurements in very different fields is another step in the right direction. One of the first objects of scientific control must necessarily be to find some quantitative measure or parallel of properties which are ordinarily judged by practice or experience, and the viscosity of sols and suspensions is such a quantity, which stands in a definite relation to qualities as difficult to define as the "nerve" of rubber or the "strength" of flour. The viscosity of rubber sols (p. 97) and the remarkable parallelism in the viscosities of sols of cellulose and of its esters (p. 94) have been mentioned already. The viscosity of suspensions of flour in water has been investigated by Lüers and Ostwald (*Koll.-Zeitschr.*, *25*, 82, 116, 1919) who find that, other things being equal, flours of good baking quality give considerably higher viscosities than those of poor quality. Incidentally other problems

connected with the properties of bread have been studied from the point of view of colloid chemistry by these authors, by Katz and others (see the article by R. Whymper in the Third British Association Report, 1920). In the modern industries dealing with cellulose and its esters, *e.g.*, the manufacture of artificial silk, nitrocellulose explosives and celluloid, viscosity determinations have been a means of control probably from the outset. Similarly some measure of the adhesive properties of glue is obtained by determining the viscosity of the sol and the "jelly strength," *i.e.*, by roughly measuring the modulus or elastic limit of the gel.

While the phenomena of swelling have been studied chiefly in their biological aspect, work on the technical side has not been wanting. The swelling of starch and of gluten, and the further changes undergone by their gels during baking and ageing, have received consideration in the investigations on bread which have already been quoted. In tanning swelling plays a part of great importance and this aspect of the subject has been studied by Procter and his school. Problems involving the degree of dispersity and the electric condition of such tanning agents as tannin also arise in this industry and are beginning to receive attention.

The effect of mere changes in the degree of dispersity on the physical and chemical behaviour of given systems has been known empirically in many arts, as well as methods of controlling it. The ripening of photographic emulsions, *e.g.*, involving a decrease in the dispersity of the particles of silver haloid, has long been known and controlled; the theoretical aspect of the processes involved is receiving a good deal of study since the methods of colloid chemistry have been applied to the problems involved. The connection between dispersity and colour is of importance in products differing as widely

as glass coloured by gold, copper or selenium on the one hand, and artificial ultramarine on the other, the colour of which is now, on very strong grounds, ascribed to sulphur in a highly disperse state. Every chemist is familiar with the methods used for making certain precipitates less disperse, so that they can be retained by filtration, and the rationale of the methods used, as well as their extension to fresh cases, will be clear to any one who has studied the formation of sols, and their coagulation.

Advantage has been taken of the electric charge on disperse particles in other directions. Electro-endosmosis and cataphoresis have been developed on a technical scale and important results in the purification of clays, dehydration of peat, etc., have been claimed. While the scientific interest of these applications is considerable, their technical success will no doubt depend on purely economic factors, like the cost of electrical energy at a given place. Cataphoresis has also been employed for the separation of oil from oil-water emulsions (condensed water), the process being carried out between iron electrodes and complicated by the formation of oxides.

It is probably unnecessary to extend this list, as every reader engaged in technical work can add to it problems which he has encountered. Nor will he have failed to notice that many fundamental points in theory still require elucidation. In both directions there is an unlimited field for work, and to the student this should, perhaps, be not the least attractive feature of a fascinating branch of physical science.

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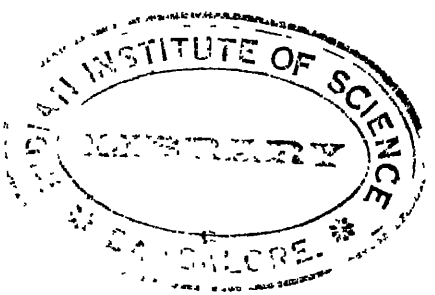
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